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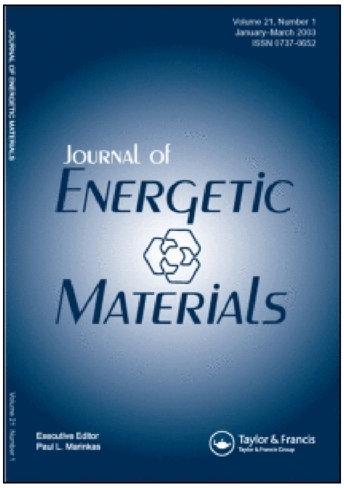

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Structure-Impact Sensitivity Relation of Certain Explosive Compounds

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Structure-Impact Sensitivity Relation of Certain Explosive Compounds

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A theoretical model is developed within the Hückel molecular orbital theory for the structure-impact sensitivity relation of some explosive compounds. The model considers some topological properties of a given molecule as well as the number of certain substituents. Also, a regression equation has been obtained for polynitrobenzenes having a high degree of significance. In light of the equations developed, effects of factors on impact sensitivity are discussed.

Keywords: explosives, impact sensitivity, polynitro benzenes, structure-activity relationship, topology

Introduction

Hot spots, proposed by Bowden and Yoffe [1,2] are small regions in the crystal lattice in which some portion of the energy gained by impact or shock is localized there. This energy may be sufficiently channeled to induce molecular vibrations that trigger the exothermic decomposition or detonation of the material [3,4]. Any dissipation of hot spot energy, such as by diffusion, lessens the likelihood of detonation. Kamlet

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proposed that free rotation around a trigger linkage can have a desensitizing effect because in this way energy is consumed that could otherwise initiate bond rupture [5,6]. Extensive work has suggested that some shock-induced reactions in condensed materials are a result of nonthermal processes [7–9]. It has been pointed out that molecular structure has an influence on the susceptibility to shock- and impact-induced reactivity [10]. It seems that nitro aromatics have a higher susceptibility to reaction of that sort than aliphatic compounds [7].

The relationship between shock-induced reactivity in an homologous series of nitro aromatics and molecular structure using a number of empirically derived parameters, such as electron donating ability of substituted groups, bond strengths as wells as molecular orbital features of the compounds (at the CINDO level) were studied by Owens [7]. Kamlet proposed that $C-NO_2$ and $N-NO_2$ bonds in explosives play the trigger role because usually they are the weakest in the molecule [11,12]. Accordingly, there have been a number of attempts to correlate sensitivity with some properties of $C-NO_2$ and $N-NO_2$ bonds [11,13].

Many efforts have been made to correlate detonation-related properties with chemical composition or structure [5,6,14–18]. Although some success has been achieved to correlate the strengths of $C-NO_2$ and $N-NO_2$ bonds to detonation properties, it is obvious that other molecular factors or reactive behavior should be important in determining sensitivity.

Theory

Explosive materials are characterized with certain instability, and the topology of a molecule is one of the factors that dictate its energy content. For example, attachment of nitro group(s) suitably to a stable π-system may engender an unstable non-Kekulé structure [19,20]. Most of the explosives having conjugated π-skeletons are of that kind; e.g., picric acid, tetryl, TNT, etc. Note that non-Kekulé structures are alternant π-systems having $n^* - n^\circ \geq 2$, where n^* and n° are the numbers of alternating starred and unstarred positions in the π-skeleton of the system considered [19]. In the cases of even and odd alternant systems, $n^* - n^\circ = 0$ and $n^* - n^\circ = 1$, respectively (e.g., benzene is an even alternant hydrocarbon system with $n^* = n^\circ = 3$ but benzyl system is odd).

Now, suppose $G(N,e)$ is the molecular graph of an alternant hydrocarbon having N vertices and e edges. Let $X_1, \ldots, X_N$ be the graph spectrum of $G(N,e)$ [21]. It is known that within the Hückel molecular orbital frame work, the total π-electron energy of a molecule is given by [22]:

$$E_\pi = \sum_{i=1}^{occ} g_i X_i \tag{1}$$

where X_i is the molecular orbital energy (in β units) of molecular orbital ψ_i and g_i is the occupancy number (number of electrons present) of that orbital [22].

It is also proved that (see Appendix 1) for alternant hydrocarbons,

$$E_\pi = 2\sqrt{\sqrt{4ma_4}\cos\lambda + e} \tag{2}$$

$$a_4 = \frac{e^2 - e}{2} - V_2 - 3V_3 - 2R_4 \tag{3}$$

$$m = \frac{n^2 - n}{2} \tag{4}$$

where a_4 is the fourth coefficient in the secular polynomial $P(X)$ of the alternant hydrocarbon whose molecular graph is $G(N,e)$ [21,23]. Note that $N = 2n$ for even alternant systems and if N is odd then n has to be taken as $n = (N+1)/2$ (see the Appendix). Whereas V_2, V_3, and R_4 are the vertices (atoms) having degree (number of bonds incident to that atom) 2, 3 and the number of four membered rings, respectively [23]. Although e, m are terms for the gross topology of the system, a_4 and $\cos\lambda$ reflect the fine topology of the molecule. Since $\cos\lambda \leq 1$ one obtains inequality (5) from Eq. (2).

$$E_\pi \leq 2\sqrt{\sqrt{4ma_4} + e} \equiv 2T \tag{5}$$

Now consider $G'(N,e)$, graph of a molecule which contains some hetero atoms. Note that $G'(N,e)$ and $G(N,e)$ contain an equal number of vertices and edges (chemically speaking the number of atoms and bonds, respectively). Topologically $G'(N,e)$ is obtained from $G(N,e)$ by replacing certain carbon atoms by heteroatoms (centric perturbations).

In the perturbation molecular orbital theory, the jth molecular orbital energy (ε_j') of a perturbed system is approximately given by [22]:

$$\varepsilon_j' = \varepsilon_j + \sum_\rho c_{j\rho}^2 \delta\alpha_\rho + 2\sum_{\rho\sigma} c_{j\rho} c_{j\sigma} \delta\beta_{\rho\sigma} \tag{6}$$

where $c_{j\rho}$ and $c_{j\sigma}$ are the jth molecular orbital coefficients of the unperturbed system at sites ρ and σ, respectively. The terms $\delta\alpha_\rho$ and $\delta\beta_{\rho\sigma}$ stand for variations in the Coulomb and resonance integral values due to carbon-heteroatom replacement. Note that a set of centric perturbations at these sites engender the perturbed structure, namely, the isoconjugate system having heteroatoms at those sites. (Note that an isoconjugate system is a hydrocarbon structure possessing the same σ-skeleton and the same number of π-electrons with the heterosystem considered.) The second summation is over all the perturbed bonds $\rho\sigma$.

Assuming that all the occupied orbitals are doubly occupied ($g_i = 2$), then using Eq. (6) one gets

$$E_\pi' = E_\pi + 2\sum_j^{occ}\sum_\rho c_{j\rho}^2 \delta\alpha_\rho + 4\sum_j^{occ}\sum_{\rho\sigma} c_{j\rho} c_{j\sigma} \delta\beta_{\rho\sigma} \tag{7}$$

The second term in Eq. (7) can be written as

$$2\sum_j^{occ}\sum_\rho c_{j\rho}^2 \delta\alpha_\rho = \sum_\rho \delta\alpha_\rho \sum_j^{occ} 2c_{j\rho}^2 \tag{8}$$

For alternant hydrocarbons $\sum_j^{occ} 2\ c_{j\rho}^2 = 1$ [22] so Eq. (8) becomes

$$2\sum_j^{occ}\sum_\rho c_{j\rho}^2\delta\alpha_\rho = \sum_\rho \delta\alpha_\rho \tag{9}$$

Similarly,

$$4\sum_j^{occ}\sum_{\rho\sigma} c_{j\rho}c_{j\sigma}\delta\beta_{\rho\sigma} = 2\sum_{\rho\sigma}\delta\beta_{\rho\sigma}P_{\rho\sigma} \tag{10}$$

where $P_{\rho\sigma}$ is the respective π-bond order. Hence, E'_π becomes

$$E'_\pi = E_\pi + \sum_\rho \delta\alpha_\rho + 2\sum_{\rho\sigma} P_{\rho\sigma}\delta\beta_{\rho\sigma} \tag{11}$$

Note that $0 \le |P_{\rho\sigma}| \le 1$. The form of summations in Eq. (11) enables one to express them as atomic or group contributions. Thus, for a typical explosive material Eq. (11) can be written as

$$E'_\pi = AE_\pi + Bk_{NO_2} + Ck_{NH_2} + Dk_X + S \tag{12}$$

where $k_{\mathrm{NO_2}}$, $k_{\mathrm{NH_2}}$ and k_X are the numbers of NO_2, NH_2, and any heteroatom (not considered in $k_{\mathrm{NO_2}}$ and $k_{\mathrm{NH_2}}$), respectively, whereas A, B, C, D, and S are the regression coefficients which can be obtained by regression analysis of Eq. (12) using experimental values.

Inserting Eq. (5) into Eq. (12) for E_π and with new values of the regression coefficients A, B, C, D, and S, a new equation can be obtained.

$$E'_\pi = A\sqrt{\sqrt{4ma_4} + e} + Bk_{NO_2} + Ck_{NH_2} + Dk_X + S \tag{13}$$

Within the Hückel molecular orbital theory, the total π-electron energy is associated with the stability of the system considered [22,24]. On the other hand, impact sensitivity of an explosive material should have an inverse relationship with the stability of that molecule. Hence, the total π-electron energy also should contribute inversely (at least in part) to the impact sensitivity.

Therefore, the regression Eq. (13) can be used for the impact sensitivities (h, measured as drop height) of a series of compounds with new values of regression coefficients A, B, C, D, and S; that is,

$$h = A\sqrt{\sqrt{4ma_4} + e} + Bk_{NO_2} + Ck_{NH_2} + Dk_X + S \qquad (14)$$

Results and Discussion

To evaluate the regression coefficients of Eq. (14), experimental impact-sensitivity data (h) for a group of explosive compounds are required. However, in the literature those data vary from one laboratory to the other. In the present study, the impact sensitivity data of trinitro benzene derivatives were excerpted from the literature [7,25]. These molecules are shown in Fig. 1 and their isoconjugate structures are presented in Fig. 2. To construct the isoconjugates the heteroatom model for methyl groups [24] has been adopted. The carboxylic acid group in the structure of compound 5 is isoconjugate with an NO_2 group but its effect is less than that. Because of that COOH group in the model has been considered as a nitro group but its contribution to k_{NO_2} was taken as 0.5 indicating that COOH is less effective than NO_2 group. Figure 3 shows an example for application of the model to get the input data. Figure 4 shows the structures of the nitramines considered presently. The calculated initial data and the excerpted h values are given in Table 1.

As pointed out in the Theory section, whenever the isoconjugate model contains an odd number of vertices, the formula $n = (N+1)/2$ was used (see Appendix 1 for its justification). Note that the impact sensitivity data presently used are all from the same laboratory [7,25]. The results of the multivariable regression analysis are shown in Table 2. As seen in the table, the regression equation has a very high R^2 (the coefficient of multiple determination [26,27]) value. The F-test for the overall significance of the regression results $F_{4,5}$ (calc.) as 158.98, whereas the tabulated values at 5% and 1% level of significance are 5.19 and 11.39 [26,27], respectively. Thus the regression equation and the hypothesis are acceptable. When the simple regression

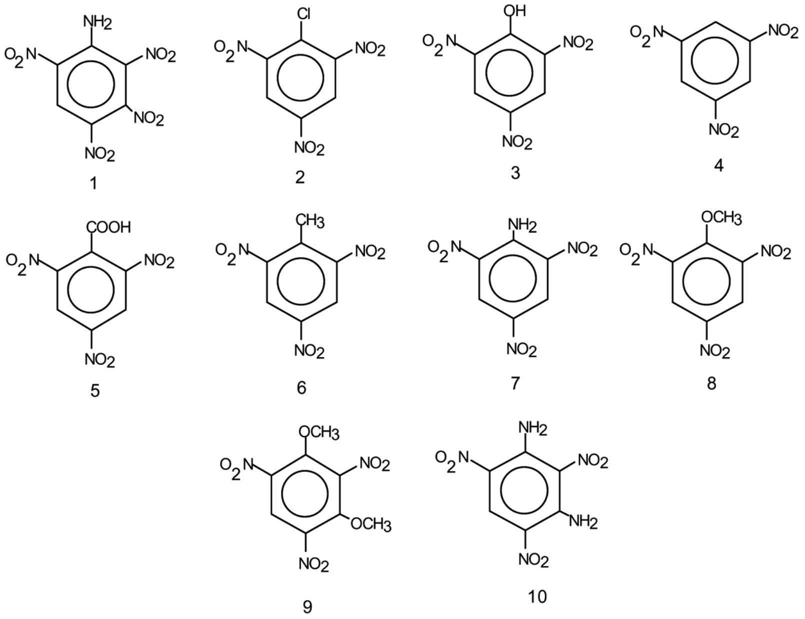

Figure 1. The structure of molecules presently considered.

coefficients r_{YX_1}–r_{YX_4} (note that X_1–X_4 stand for the independent variables T, k_{NO2}, k_{NH2}, and k_X in Eq. (14), whereas Y is the dependent variable, h, the impact sensitivity) are considered,

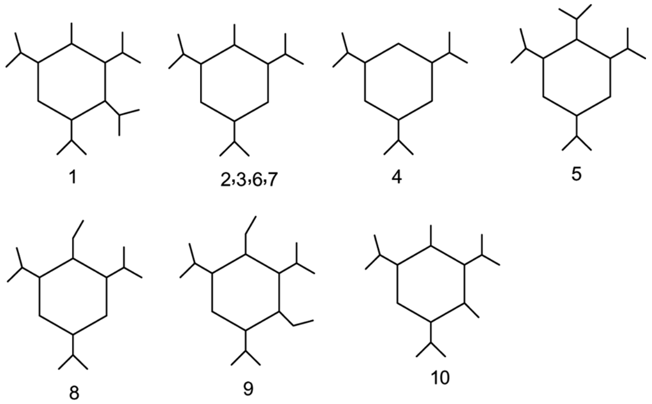

Figure 2. The models used for the regression.

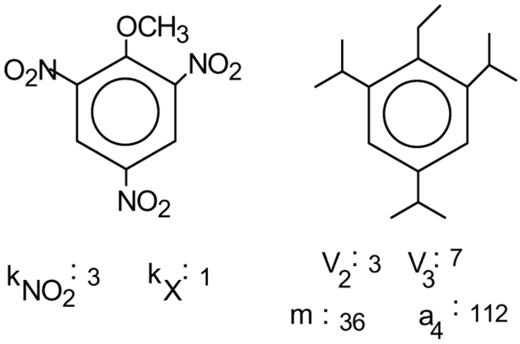

Figure 3. An example for the calculations.

the sensitivity is mainly correlated with the number of NO_2 groups (r_{YX_2}: −0.5). The effect of NH_2 groups is opposite to the NO_2 substituents (r_{YX_3}: 0.46). The topological effects predicted by terms expressed in Eq. (5) and the effects of hetero atoms other than ones in NO_2 and NH_2 groups are comparable in the same direction and moderate in magnitude.

On the other hand, inspection of the regression coefficients r_{XiXj} reveals that the independent variable, the topological term, and k_{NO_2} have some tendency to be moderately collinear. This is

Table 1
The input data for the regression analysis ($T = \sqrt{\sqrt{4ma_4} + e}$)

No.	T	k_{NO_2}	k_{NH_2}	k_X	h (cm) [7,25]
1	13.39	4	1	0	41
2	10.96	3	0	1	79
3	10.96	3	0	1	87
4	10.58	3	0	0	100
5	12.37	3.5	0	0	109
6	10.96	3	0	0	160
7	10.96	3	1	0	177
8	11.99	3	0	1	192
9	13.41	3	0	2	251
10	11.97	3	2	0	320

Table 2
The statistical output data for the regression

$h = A\sqrt{\sqrt{4ma_4} + e} + Bk_{NO_2} + Ck_{NH_2} + Dk_X + S$
$Y = AX_1 + BX_2 + CX_3 + DX_4 + S$

The regressed coefficients

A	B	C	D	S
103.5566	−391.0274	28.7526	−74.3699	192.0235

$\mathrm{R}^2 : 0.992198\ \mathrm{F}_{4,5}(5\%) = 5.19, \mathrm{F}(\text{calc.}) = 158.98$
$F_{4,5}(1\%) = 11.39$

Simple correlation coefficients
$Y{:}h, X_1{:}T, X_2{:}k_{NO2}, X_3{:}k_{NH2}, X_4{:}k_X$

r_{YX1}	r_{X1X2}	r_{X1X3}	r_{X1X4}	r_{YX2}	r_{X2X3}	r_{X2X4}	r_{YX3}	r_{X3X4}	r_{YX4}
.17915	.61471	.19535	.29232	−.50429	.18835	−.34921	.46429	−.44946	.18612

quite normal because each NO_2 substituent attached to the ring increases the V_3 component of a_4 by two units. When $D = Y_{\text{obs}} - Y_{\text{calc}}$ values are considered, the percentage error is at most 14.5 (in absolute value) just for one case and for the rest is ca. 5%.

Inherently, the coefficient of the topological term is a positive quantity, which means that as this term grows, the structure becomes more and more stable; thus, h (drop height) increases and hence the sensitivity decreases. The topological term increases with any of the components e, m, and a_4 (see Eqs. (2) and (5)). The first two are related to the size of the system. Indeed, high-molecular-weight aromatic compounds have been recognized for their high thermal stability [28]. Also, conjugation between aromatic rings is known to increase thermal stability in explosives [28]. For instance, HNS (2,2′,4,4′,6,6′-hexanitrostilbene), which is derived from TNT, is more stable than its precursor. HNAB (2,2′,4,4′,6,6′-hexanitroazobenzene) is another example of that sort. In all these explosives, the major factor contributing to stability is the topological factor (T) of Eq. (13). On the other hand, branching increases V_3 and thus decreases a_4. Thus, being the others same the sensitivity should increases with branching because stability decreases. By certain topological variations a compound can be converted to its various isomers. Then any increase in V_2 should also increase the sensitivity but less than the increase in V_3 component. Note that in most of the isomers as V_3 increases, V_2 decreases. However, V_3 is more effective than V_2 as seen in

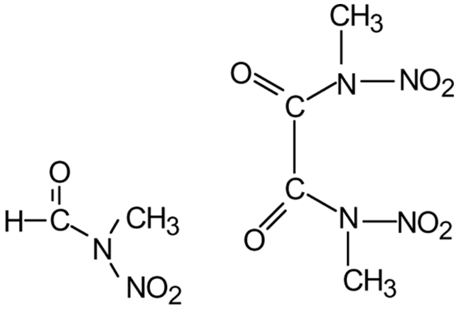

Figure 4. Structures of the nitramides considered.

Eq. (3). Although R_4 is zero for the presently considered systems, the effect of four-membered rings is more than the effect of V_2 but less than V_3. The above discussion about the effect of branching should be valid for other systems isoconjugate with certain alternant hydrocarbons. In the present specific case, the signs of the regression coefficients for $k_{\mathrm{NO_2}}$ and $k_{\mathrm{NH_2}}$ reveal that the sensitivity increases with the number of NO_2 groups but decreases with NH_2 groups. The fourth regression coefficient, D, is a negative number; thus, any hetero atom like active halogens (F, Cl) or oxygen (for which −I effect is more pronounced than +M effect) should increase the impact sensitivity.

The present approach can be extended to other types of molecules including heterocycles or nitramines as long as the isoconjugate systems of their π-skeletons are alternant hydrocarbons (even or odd). However, there has to be some resemblance between the structures considered; namely, cyclic molecules and acyclic ones should not be included in the same group for the regression. The best set of molecules should comprise isomeric structures having similar gross topology but differing in fine topology as the presently considered polynitro benzene derivatives. Otherwise, some deviations occur, although in some cases relative order of sequence can be predicted correctly. For example, N-nitro-N-methyl-formamide and N,N′-dimethyl-N,N′-dinitrooxamide have h values of 320 and 79 cm, respectively [29]. Equation (14), with regression coefficients given in Table 2, estimates h values for the above-mentioned explosives as 125 and 78 cm, respectively (in the calculations $k_{\mathrm{NO_2}}$: 1, $k_{\mathrm{NH_2}}$: 1, k_X: 1, and $k_{\mathrm{NO_2}}$: 2, $k_{\mathrm{NH_2}}$: 2, k_X: 2 are used for these nitramide-type explosives).

Conclusion

The presently developed model gives some insight regarding how topological and substituent effects contribute to the impact sensitivity of systems isoconjugate with certain alternant hydrocarbons. Although the regression equation is obtained for trinitro benzenes, the model based on the perturbation molecular orbital theory within the Hückel molecular orbital approach is general and Eq. (14) can be regressed for some other types of explosives. The present work could also be useful for the design of novel explosives starting from topological grounds.

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Appendix 1

Consider an even alternant hydrocarbon system having $N=2n$ atoms and e bonds in its π-skeleton. Its total π-electron energy E_π is

$$E_\pi = 2\sum_{i=1}^{n} X_i \tag{A1}$$

where X_{i} is the occupied molecular orbital energy. Squaring both sides,

$$\mathrm{E}_\pi^2 = 4\left(\sum_{i=1}^{n} X_i^2 + 2\sum_{i\prec j}^{n} X_i X_j\right) \tag{A2}$$

Since for alternant hydrocarbons $\sum_{i=1}^{n} X_i^2 = e$ [22], Eq. (A2) can be written as

$$E_\pi^2 = 4\left(e + 2\sum_{i\prec j}^{n} X_i X_j\right) \tag{A3}$$

Note that the number of terms in the summation is equal to

$$m = \frac{n^2 - n}{2} \tag{A4}$$

Suppose $P(X)$ is the characteristic polynomial of the even alternant hydrocarbon having $N=2n$ atoms and e bonds, then

$$P(X) = X^{2n} + a_1X^{2n-1} + \ldots + a_{2n-1} + a_{2n} \tag{A5}$$

Now, let E_m be an m-dimensional Euclidean space [30] and vectors **C** and **D** defined as

$$\mathbf{C}(X_1X_2, X_1X_3, \ldots, X_{n-1}X_n)\ \mathbf{D}(1, 1, \ldots, 1)$$

where $X_1, X_2, \ldots, X_n$ are the roots (counting multiplicities) of the characteristic polynomial $P(X)$ and standing for the occupied molecular orbital energies (in β units) of the molecule. Note that the number of components of vectors **C** and **D** is m. The scalar product of these vectors is

$$(C, D) = \sum_{i \prec j}^{n} X_iX_j \tag{A6}$$

$$(C, D) = \|C\|\|D\| \cos\lambda \tag{A7}$$

where λ is the angle between vectors **C** and **D**. On the other hand,

$$\|C\| = \sqrt{\sum_{i \prec j}^{n} X_i^2X_j^2} \tag{A8}$$

Since $a_4 = \sum_{i \prec j}^{n} X_i^2X_j^2$ [23,31], $\|C\| = \sqrt{a_4}$, whereas $\|D\| = \sqrt{m}$. Thus,

$$(C, D) = \sqrt{ma_4}\cos\lambda \tag{A9}$$

Combining Eqs. (A6) and (A9)

$$\sum_{i \prec j}^{n} X_iX_j = \sqrt{ma_4}\cos\lambda \tag{A10}$$

Inserting Eq. (A10) into (A3), taking the square root and simplifying one obtains,

$$E_\pi = 2\sqrt{\sqrt{4ma_4}\cos\lambda + e} \tag{A11}$$

Odd alternant hydrocarbons possess a nonbonding molecular orbital (NBMO) whose energy (X_{n+1}) is zero [22,24]. Let $N = 2n + 1$ be the number of atoms in an odd alternant hydrocarbon. Then,

$$\sum_{i \prec j}^{n+1} X_i X_j = \sum_{i \prec j}^{n} X_i X_j + X_n X_{n+1} \tag{A12}$$

Since $X_{n+1} = 0$ (NBMO energy), the last term in (A12) vanishes. Thus the expression (A8) is valid for the norm of **C** irrespective of the odd or even nature of the alternant hydrocarbon, although **C** in the case of an odd alternant system has $n + 1$ components and thus $m = (n^2 + n)/2$.