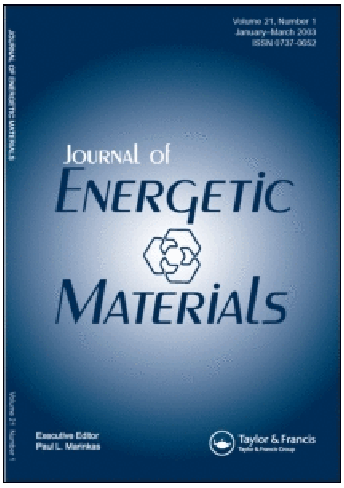


Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

Theoretical Investigation of the Relationship between Impact Sensitivity and the Charges of the Nitro Group in Nitro Compounds

Zhang Chaoyang[a]; Shu Yuanjie[a]; Huang Yigang[a]; Wang Xinfeng[a]
[a] China Academy of Engineering Physics, Institute of Chemical Materials, Sichuan, People's Republic of China

To cite this Article Chaoyang, Zhang , Yuanjie, Shu , Yigang, Huang and Xinfeng, Wang(2005) 'Theoretical Investigation of the Relationship between Impact Sensitivity and the Charges of the Nitro Group in Nitro Compounds', Journal of Energetic Materials, 23: 2, 107 — 119

To link to this Article: DOI: 10.1080/07370650590936433

URL: http://dx.doi.org/10.1080/07370650590936433

Energetic Materials, 23: 107–119, 2005
Copyright © Taylor & Francis Inc.
ISSN: 0737-0652 print
DOI: 10.1080/07370650590936433

Theoretical Investigation of the Relationship between Impact Sensitivity and the Charges of the Nitro Group in Nitro Compounds

ZHANG CHAOYANG
SHU YUANJIE
HUANG YIGANG
WANG XINFENG

Institute of Chemical Materials, China Academy
of Engineering Physics, Sichuan, People's
Republic of China

By means of density functional theory (DFT), the general gradient approximation method (GGA), and the Beck LYP hybrid functional and DNP basis set, nitro group Mulliken charges ($\mathbf{Q_{NO_2}}$) *are calculated and defined to assess and correlate with the impact sensitivities* ($\mathbf{H_{50}}$) *of nitro compounds: very negative* $\mathbf{Q_{NO_2}}$ *and high* $\mathbf{H_{50}}$*. By calculating, analyzing, and comparing, we find that* $\mathbf{Q_{NO_2}}$ *can be regarded as a structural parameter to estimate impact sensitivity and has more availability in almost all nitro compounds in contrast to the length of the* $C{-}NO_2$, $N{-}NO_2$, *or* $O{-}NO_2$ *bond* $\mathbf{R_{R-NO_2}}$*, molecular electrostatic potential* ($\mathbf{V_{mid}}$)*, and oxygen balance* (**OB**)*. At the same time, it has good reliability and accuracy even though there are some exceptions. According to the data in this paper, the compound may be sensitive* ($\mathbf{H_{50}} \leq 0.4\,m$) *when its nitro group has fewer negative charges than about 0.23.*

Address correspondence to Zhang Chaoyang, Institute of Chemical Materials, China Academy of Engineering Physics, Mianyang, Sichuan 621900, People's Republic of China. E-mail: zcy19710915@yahoo.com.cn

Keywords: nitro compounds, charges of nitro group, impact sensitivity

1. Introduction

The relationship between the sensitivity and molecular structure of high-energy density materials (HEDMs) has become an important subject. The ''trigger linkage'' is a common but very important concept that considers that a bond rupture is the key step in detonation initiation. Many researchers believe that $C{-}NO_2$, $N{-}NO_2$, and $O{-}NO_2$ bonds are trigger spots in nitro compounds. Depluech and Cherville [1–3] propose that shock wave and thermal sensitivities in nitro compounds can be related to the electronic structure of the molecule and properties of $C{-}NO_2$, $N{-}NO_2$, and $O{-}NO_2$ bonds such as electrostatic potentials, lengths, strengths, etc. Xiao [4] suggests that the stronger these bonds, the more stable the molecules. Bates [5], however, thinks that the sensitivity of tetrazole is related to the ability of substitution groups to attract electrons: the stronger the ability is, the more sensitive the compound is. Kamlet and Adolph [6] draw a conclusion that the impact sensitivity of some nitro compounds can increase as their oxygen balances are enhanced. Politzer concludes that sensitivity must be related to the molecular surface electrostatic potential, and more detailed overviews are presented in his paper [7]. But these criteria and correlation methods often meet ''abnormal'' cases or have a certain limitation. Additionally, Zeman's work is very noticeable for its correlation between the characteristics of impact and electric spark sensitivities, detonation and thermal decomposition, and ^{13}C and ^{15}N NMR chemical shifts of polynitro compounds [8].

After performing many calculations, the authors of this paper find that the relationship between the impact sensitivities and electronic structures of $C{-}NO_2$ compounds can be established by charge analysis of the nitro group, and we try to extend this method to all nitro explosive compounds.

2. Theory and Computational Details

In the chemical world, there is a common rule that a state with higher potential can convert into another one with lower potential automatically, and the system becomes more stable. For example, an oxidant with high oxidizing potential and a reducer with high reducing potential can easily react with each other and convert into product(s) with lower relevant potentials, and the total system (including oxidant and reducer) becomes more stable. There are the same cases in the covalent compounds. Covalent compounds are composed of atoms or groups that have the potential to offer or attract electrons, and they will be more stable if the atoms or groups offer or attract adequate electrons. Hydrides such as HF, H_2O, NH_3, and CH_4 are taken as examples, and relevant calculation results of them are listed in Table 1. In these hydrides H atoms have potentials to offer electrons. There are some consistent orders in these hydrides: bond homolysis energies, Pauling electronegativities (**x**) of central atoms (F, O, N, and C atoms), and Mulliken charges on H atoms decrease, and bond lengths increase as follows (in fact, people usually use these parameters to estimate the molecular stability): $HF > H_2O > NH_3 > CH_4$. So we can find that H atoms in different hydrides have different abilities to offer electrons, and we can assess hydrides' stabilities not only by electro-negativities of central atoms, bond properties, but also by charges of common atoms in hydrides:

Table 1
Relevant content of some hydrides

Hydride (RH_n)	HF	H_2O	NH_3	CH_4
Homolysis energy of the first H-R bond(298 K), kJ/mol	557.16	480.60	434.08	433.47
H-R bond length, Å	0.925	0.965	1.018	1.091
Pauling **x** of R atom	3.98	3.44	3.04	2.55
Mulliken charge on H atom, **e**	0.358	0.305	0.239	0.118

H atoms; that is, the hydrides will become more stable when their H atoms offer more electrons and have more positive charges. Here H atoms' potentials to offer electrons are represented by their Mulliken charges. Namely, the more positive charges the H atoms have, and the more their potentials decrease, the more stable the hydrides become.

As for nitro groups in nitro compounds, they are very strong for attracting electrons, that is, they have large potentials for attracting electrons. The same as the potentials of H atoms in the above hydrides, these potentials can also be represented by charges of the nitro group, but not only of a different atom. Similarly, we can draw a primary and tentative conclusion similar to the former: the more negative charges the nitro groups have, and the more their potentials decrease, the more stable the nitro compounds become. Certainly, the ‘‘hot spot’’ theory and ‘‘trigger linkage’’ concept are accepted in this paper. In nitro covalent compounds, $C-NO_2$, $N-NO_2$, $O-NO_2$ bonds (called $R-NO_2$ bond; for poly-nitro-compounds, the weakest bonds are discussed and showed in a circle in Figure 1) are the feeblest in the entire molecule, and their ruptures are the initial steps in the decomposition or detonation. Moreover the impact sensitivities are used to show the stabilities of nitro compounds. To verify the conclusion, that is, to answer the questions ‘‘Is there a relationship between the nitro group charges and the stabilities (for example, impact sensitivities) of compounds and what is the relationship?,’’ Mulliken charges of nitro groups and relevant atoms, $R-NO_2$ bond lengths of nitro substitutes of methane and nitro compounds in Figure 1 are calculated. All calculations are performed with the Acceryls' Dmol^3 code, and the General Gradient Approximation method (GGA) and Beck LYP hybrid functional and DNP basis set are adopted. At the same time, some comparisons and analyses are performed by Politzer's method and an oxygen balance method we have defined. The oxygen balances (**OB**, according to product CO_2) of nitro compounds $C_aH_bO_cN_d$ can be calculated by Equation (1); and nitro group charges ($\mathbf{Q_{NO_2}}$) are calculated by Equation (2), where Q_N, Q_{O1}, and Q_{O2} are charges of N and O atoms on the nitro group, respectively; and molecular

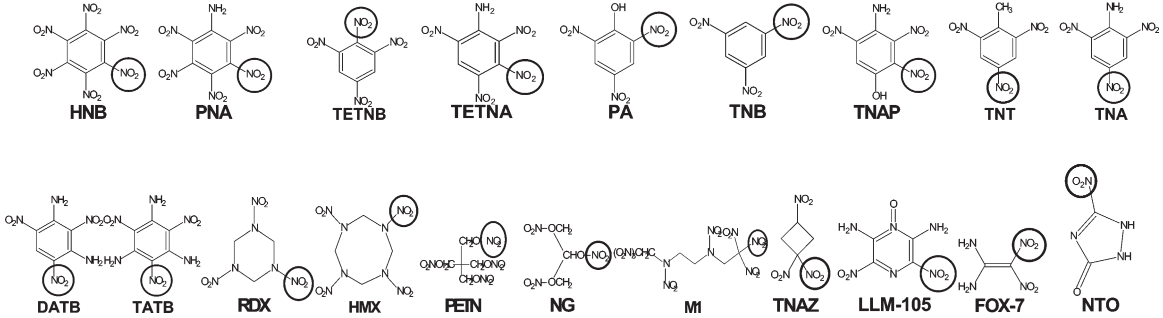


Figure 1. Nitro compounds discussed in this paper.

electrostatic potentials (**V_{mid}**, the largest molecular electrostatic potential **$V_{mid,max}$** is adopted) by Equation (3) according to Politzer's suggestion, where Q_R is the charges of the C or N or O atoms, joined with the nitro group, $Q_{N(NO_2)}$ is the charges of the N atom on the nitro group, and R_{R-NO_2} is the bond length of the $R-NO_2$ bond.

$$OB(CO_2) = \frac{c - (2a + b/2)}{2a + b/2} \times 100\%, \tag{1}$$

$$Q_{NO_2} = Q_N + Q_{O1} + Q_{O2}, \tag{2}$$

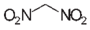
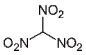
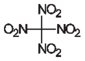
$$V_{mid} = \frac{2(Q_R + Q_{N(NO_2)})}{R_{R-NO_2}}. \tag{3}$$

3. Results and Discussion

3.1. Nitro Substitutes of Methane

Usually the more substituted the nitro group, the less stable the compound. Methane is taken as an example in Table 2. It can be found that negative charges of the nitro group decrease and the $R-NO_2$ bond length, **V_{mid}**, and **OB** increase in the same order when the substituted nitro groups increase from the table. When the number of the nitro group increases, offering electrons become more and more difficult because H atoms,

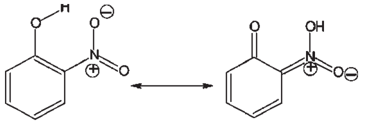
Table 2
Relevant calculation results of nitro substitutes of methane

Compounds s	H_3C-NO_2			
Q_{NO_2}, e	−0.285	−0.192	−0.152	−0.050
R_{R-NO_2}, Å	1.517	1.543	1.548	1.582
V_{mid}	0.123	0.185	0.227	0.244
$OB(CO_2)$	−42.87%	33.33%	140.00%	300.00%

which offer electrons, become fewer and fewer. Meanwhile, the nitro group's potentials to attract electrons decrease to less and less, and the compound becomes more and more unstable accordingly. As a result, for nitro-substituted methane, $\mathbf{Q_{NO_2}}$, can be used to assess the stabilities of compounds as $\mathbf{R_{R-NO_2}}$, $\mathbf{V_{mid}}$, and **OB**.

3.2. Nitroaromatic Molecules

Nitroaromatic compounds from [9] are also calculated for verifying that there is a relationship between impact sensitivities ($\mathbf{H_{50}}$) and $\mathbf{Q_{NO_2}}$, **OB**. The results are listed in Table 3 and Figure 2. The relationship between $\mathbf{H_{50}}$ and $\mathbf{Q_{NO_2}}$ shows us an obvious tendency: the more negative the $\mathbf{Q_{NO_2}}$, the more $\mathbf{H_{50}}$: that is, the more negative charges the nitro group has, the more stable and insensitive the compound is. But there are two exceptions—two nitro-phenols, PA and TNAP (TNB and TNT can also be seen as two exceptions). These exceptions can be explained using Politzer's suggestion. Usually a minor part of nitro-phenols (NPs) can change into nitrogen acids (NAs) as shown in Equation (4); these have higher total energies and higher sensitivities. We calculated two isomers of PA and TNAP, respectively, and found that it was indeed the case: PA: – 921.2358675 hartree (NP) and – 921.1879466 hartree (NA); TNAP: – 976.5969929 hartree (NP) and – 976.5654405 hartree (NA). So, it is no surprise that these exceptions exist: $\mathbf{Q_{NO_2}}$ is calculated according to NPs, but $\mathbf{H_{50}}$ must be of NAs.



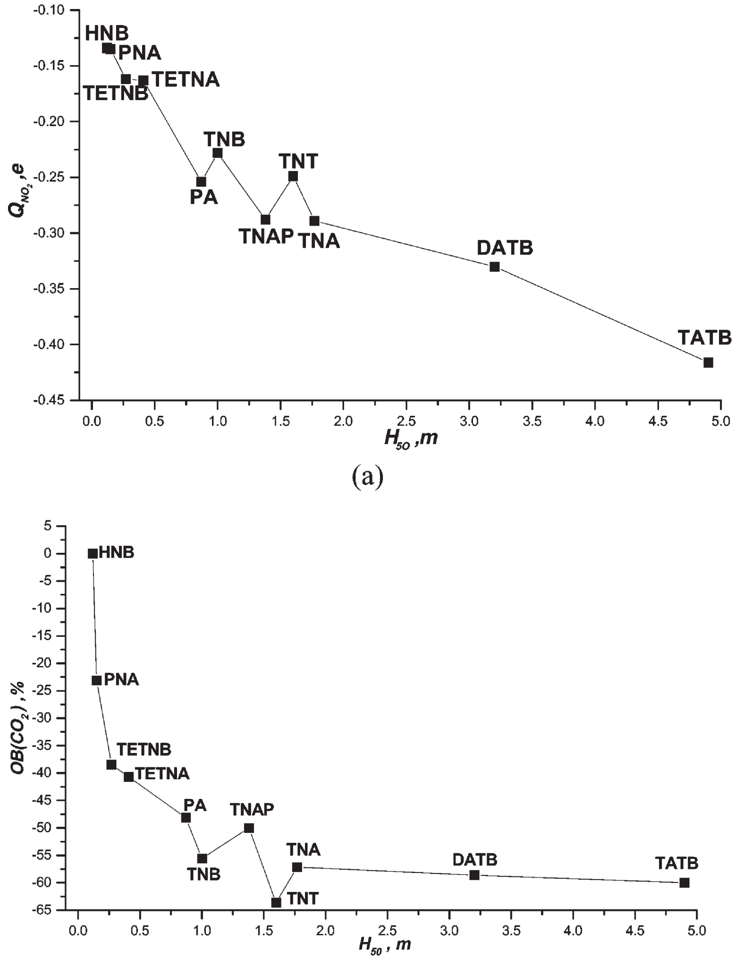
(4)

As to the correlation between $\mathbf{H_{50}}$ and **OB**, there is also a distinct tendency similar to the relationship between $\mathbf{H_{50}}$ and $\mathbf{Q_{NO_2}}$: the less **OB**, the higher $\mathbf{H_{50}}$. It means that the compound with less **OB** has higher stability and lower sensitivity. But two exceptions also exist: TNB and TNT. This must be similar to the above exceptions and due to other thermal decomposition

Table 3

Relevant calculation results of nitro-aromatic compounds

Compounds	HNB	PNA	TETNB	TETNA	PA	TNB	TNAP	TNT	TNA	DATB	TATB
$\mathbf{H_{50}}$, **m**	0.12	0.15	0.27	0.41	0.87	1.00	1.38	1.60	1.77	3.20	4.90
$\mathbf{Q_{NO_2}}$, **e**	−0.134	−0.135	−0.162	−0.163	−0.254	−0.228	−0.288	−0.249	−0.289	−0.330	−0.416
$\mathbf{R_{R-NO_2}}$, Å	1.466	1.473	1.506	1.511	1.504	1.465	1.476	1.463	1.483	1.431	1.408
$\mathbf{V_{mid}}$	0.632	0.372	0.656	0.668	0.568	0.632	0.632	0.588	0.612	0.548	0.500
OB(CO_2)	0.00%	−23.08%	−38.46%	−40.74%	−48.15%	−55.56%	−50.00%	−63.64%	−57.14%	−58.62%	−60.00%
OB(CO) [6]	3.45%	1.89%	0.78%	0.37%	−0.44%	−1.41%	−0.82%	−3.08%	−1.75%	−2.06%	−2.33%



(a)

(b)

Figure 2. Relationship between $\mathbf{H_{50}}$ and (a) $\mathbf{Q_{NO_2}}$, (b) **OB** of nitroaromatic compounds.

mechanisms. In fact, **OB** must be consistent with $\mathbf{Q_{NO_2}}$. For example, oxygen atoms or attracted-electron groups will increase when **OB** increases, and the nitro group on the weakest $R{-}NO_2$ can only attract fewer electrons. Additionally, the results calculated by our method are very consistent with [6] (see Tables 3 and 4). So this shows our method is usable, but it must be more advantageous, because it is simpler and easy to calculate.

Sometimes the shorter the $\mathbf{R_{R-NO_2}}$ is, and the stronger the $R{-}NO_2$ is, the more insensitive the compound is. For instance, TATB and DATB have smaller $\mathbf{R_{R-NO_2}}$ and higher $\mathbf{H_{50}}$. But it is not always the case. It can't be found that there is an obvious tendency from Table 3: the smaller $\mathbf{R_{R-NO_2}}$, the higher $\mathbf{H_{50}}$. It is the same as for $\mathbf{V_{mid}}$. There is no obvious correlation between $\mathbf{H_{50}}$ and $\mathbf{V_{mid}}$ according to relevant data in Table 3, even though TATB and DATB have smaller $\mathbf{V_{mid}}$ and higher $\mathbf{H_{50}}$. Some exceptions, such as PNA, exist; PNA has the lowest $\mathbf{V_{mid}}$ but not the highest $\mathbf{H_{50}}$. The authors think it is worth our while to discuss Politzer's suggestion showed by Equation (3). According to this equation, $\mathbf{V_{mid}}$ will increase, and the sensitivity of the compound will be enhanced if $\mathbf{R_{R-NO_2}}$ decreases when the summation of $\mathbf{Q}_N$ and $\mathbf{Q}_R$ keeps constant. In other words, decreasing $\mathbf{R_{R-NO_2}}$ is not helpful for decreasing $\mathbf{V_{mid}}$ and sensitivity. This must be contrary to many conventions: the shorter the $\mathbf{R_{R-NO_2}}$, and the stronger the $R{-}NO_2$, the more stability and the less sensitivity.

3.3. Other Explosive Molecules

Two main nitric ester explosives, PETN and NG, two main nitramine explosives, RDX and HMX, and other explosives are discussed in Table 4. From the table, it can be found that two nitric esters have positive nitro group charges, and this must be due to the nitro group's joining with the oxygen atom, which has more ability to attract electrons. Apparently, the nitro group's potential to attract electrons cannot decrease. Accordingly, the nitric esters are unstable and have smaller $\mathbf{H_{50}}$. Explosive molecules such as RDX, HMX, M1, and TNAZ have less than 0.12 e negative $\mathbf{Q_{NO_2}}$ and higher impact sensitivities ($\mathbf{H_{50}} \leq 0.32\,\mathrm{m}$), but other explosives such as FOX-7, LLM-105, NTO, and NQ have more negative $\mathbf{Q_{NO_2}}$ (>0.26) and higher $\mathbf{H_{50}}$ (> 0.72 m). So, for these explosive molecules, that

Table 4
Relevant contents of other nitro compounds

Compounds	PETN	NG	RDX	HMX	M1	TNAZ	FOX-7	LLM-105	NTO	NQ
H_{50}, m [10,11]	0.11	0.20	0.28	0.32	0.11	$\leq$ 0.30	0.72	1.17	2.93	$>$ 320
Q_{NO_2}, e	0.058	0.077	−0.105	−0.112	−0.051	−0.114	−0.365	−0.292	−0.264	−0.294
R_{R-NO_2}, Å	1.436	1.534	1.412	1.392	1.527	1.506	1.454	1.448	1.426	1.347
V_{mid}	0.146	0.324	0.156	0.194	0.164	0.142	0.169	0.173	0.251	0.044
OB(CO_2)	5.88%	14.29%	−33.33%	−33.33%	0.00%	−20.00%	−33.33%	−50.00%	−40.00%	−50.00%
OB(CO) [6]	1.90%	3.08%	0.00%	0.00%	2.10%	1.04%	0.00%	−0.93%	0.00%	−1.92%

the molecules have high $\mathbf{H_{50}}$ if they have low $\mathbf{Q_{NO_2}}$ can also be showed as a rule, even though there is not a corresponding relationship between $\mathbf{Q_{NO_2}}$ and $\mathbf{H_{50}}$ (for example, PETN has the least $\mathbf{H_{50}}$ but not the largest $\mathbf{Q_{NO_2}}$, and FOX-7 has the least $\mathbf{Q_{NO_2}}$ but not the largest $\mathbf{H_{50}}$).

Obviously, we cannot adopt the criterion of $\mathbf{V_{mid}}$ to assess the sensitivities of these compounds. But to show the limitation of $\mathbf{V_{mid}}$ (limits of aviations figured out in [7]), we have calculated it. Additionally, $\mathbf{R_{R-NO_2}}$ and **OB** have a rougher relation on $\mathbf{H_{50}}$ than $\mathbf{Q_{NO_2}}$, and there are many and even inverse exceptions in it.

4. Conclusions

By calculating, analyzing, and comparing, we can find that $\mathbf{Q_{NO_2}}$ can be regarded as a structural parameter to assess impact sensitivity (the low $\mathbf{Q_{NO_2}}$ and the high $\mathbf{H_{50}}$) and has more availability in almost all nitro compounds in contrast to $\mathbf{R_{R-NO_2}}$, $\mathbf{V_{mid}}$, and **OB**. At the same time it has good reliability and accuracy even though there are some exceptions. According to the data in this paper (in Tables 3 and 4), the compound may be sensitive ($\mathbf{H_{50}} \leq 0.4\,\mathrm{m}$) when its nitro group has a smaller negative charge than about 0.23.

Acknowledgments

We are very grateful for the support of CAEP funds (No. 2002Z0501 and No. 42101030404).

References

[1] Delpuech, A. and J. Cherville. 1976. *J. Proc. of the Symp. Chem. Probl. Connected Stab. Explos.*, 2: 21–28.

[2] Delpuech, A. and J. Cherville. 1978. *J. Propellants, Explosives*, 3(6): 169.

[3] Delpuech, A. and J. Cherville. 1979. *J. Propellants, Explosives*, 4(6): 121.

[4] Heming, X. 1994. *Molecular Orbital Theory of Nitro-compounds*, Peking: Publishing House of Defense Industry (in Chinese).

[5] Bates, L. R. 1986. *Proc. Symp. Explos. Protech.*, 13: I1–I10.

[6] Kamlet, M. J. and H. G. Adolph. 1979. *Prop. Explos. Pyrotech.*, 4(2): 30.

[7] Leszczynski, J., (ed). 1999. *Computational Chemistry, Reviews of Current Trends*, Singapore: World Scientific, pp. 271–286.

[8] Zeman, S. 2003. *Energetic Materials, Part 2*, ed. P. Politzer, and Jane S. Murray, Amsterdam: Elsevier, pp. 25–52.

[9] Rice, B. M. et al. 2002. *Journal of Molecular Structure (Theochem)*, 583: 69–72.

[10] Dobratz, B. M. and P. C. Crawford. 1985. *LLNL Explosives Handbook: Properties of Chemical Explosives and Explosive Simulants* (UCRL-52997-Chg.2): pp. 187–188 (translated into Chinese).

[11] Phillp, F. P., S. L. Gregory, R. M. Alexander, et al. 2002. *Thermochimica Acta*, 384: 187–204.