J. Phys. Chem. A **2006,** *110,* 14029−14035 **14029**

Investigation on the Correlation between the Interaction Energies of All Substituted Groups and the Molecular Stabilities of Nitro Compounds

Chaoyang Zhang

Laboratory of Material Chemistry, Institute of Chemical Materials, China Academy of Engineering Physics (CAEP), P.O.Box 919-327#, Mianyang, Sichuan, P. R. China (621900).

Received: June 15, 2006; In Final Form: September 12, 2006

A model, similar to an isodesmic reaction, is for the first time presented in this paper for describing, defining, and calculating the interaction energies of the indirectly linked groups or atoms within one molecule. Its applications to nitro substitutes of methane, benzene, and cubane verify its validity for a separate group of closely related compounds by the reasonable correlation between the calculated interaction energies of all substituted groups and the molecular stabilities or experimental impact sensitivities. Comparing with some existing rules of assessing the molecular stability, this so-called interaction energy is calculated using a model considering the chemical structures, that is, the electronic environments of compounds, and can be well related with the stabilities of nitro compounds. All investigation results show that the so-called interaction energy is a new, quantitative, and useful tool to evaluate the stabilities of nitro compounds

1. Introduction

The world of matter is one of interactions. Numerous phenomena such as the shifts of spectra,[1] the orientations of adsorptions and reactions,[2,3] the stability of a system,[4] and so forth, are mainly attributed to the interactions in the related systems. Interaction energy (IE), the energy difference of a system before and after interaction, can be calculated by eq 1:

$$\mathrm{IE} = \Delta E = \sum_{\mathrm{FINAL}} E - \sum_{\mathrm{INITIAL}} E \tag{1}$$

where FINAL and INITIAL denote after and before interaction, respectively. The sign of IE indicates the direction of interaction, that is, positive for repulsion and negative for attraction. From a viewpoint of chemistry, there exist three kinds of basic interactions demonstrated in Scheme 1: the interaction between two molecules (Case I), the interaction between two linked groups or atoms in one molecule (Case II), and the interaction between two indirectly linked groups or atoms within one molecule (case for the discussion in this paper, Case III). In Case I, IE between smaller molecules can be calculated accurately by a variation method with basis set superposition error treatment,[5−8] and perturbation theory,[9−11] whereas that between large molecules is generally calculated by the molecular forcefield methods, including molecular mechanics, molecular dynamics, and semiempirical quantum chemistry methods. For Case II, bond dissociation energy (BDE)[12] can be used to evaluate IE. However, for Case III, there is no report on a method to calculate the IE.

SCHEME 1. Three Types of the Simplest but Most Basic Interactions

Case I Interaction between two molecules.

$$\mathbf{M1} + \mathbf{M2} \longrightarrow \mathbf{M1} \cdots\cdots \mathbf{M2}$$

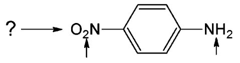
$$IE = E(M1 \cdots M2) - E(M1) - E(M2)$$

Case II Interaction between two linked groups in one molecule.

$$\mathbf{R1} + \mathbf{R2} \longrightarrow \mathbf{R1}\text{—}\mathbf{R2}$$

$$IE = E(R1 - R2) - E(R1) - E(R2)$$

Case III Interaction between two unlinked groups denoted by arrows in one molecule.



$$IE = ?$$

When indirectly linked groups or atoms within one molecule are very close to one another or on relatively appropriate positions in conjugated systems, the interactions among groups or atoms, or the effects of them, may become strong enough to affect the molecular properties.[4,13−15] We have investigated some nitro compounds, including some widely applied explosives,[14,15] and found that the interactions among amino and nitro groups can distinctly influence the nitro group charges, the bond length, and the molecular stabilities. Now, it has been confirmed that the introduction of amino groups into multinitrobenzene can lower the sensitivities of corresponding energetic materials. For example, when one, two, or three amino groups are introduced to 1,3,5-trinitrobenzene (TNB) to form 1-amino-2,4,6-trinitrobenzene (TNA), 1,3-diamino-2,4,6-trinitrobenzene (DATB), and 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), the H_{50} increases from 1.00 m to 1.77, 3.20, and 4.90 m, respectively.[16] This means that, the more amino groups are added, the lower the impact sensitivity becomes because the impact sensitivity is measured by the drop height H_{50}, from where a given weight falling upon the compound gives a 50% probability of initiating an explosion. Our calculation results showed that the amino groups on even positions relative to nitro groups can obviously increase the nitro group charges, shorten the C−nitro bond length, and increase the molecular stability in amino−nitro-substituted conjugated systems. Particularly, this effect became strongest when amino groups were on the 2-position (i.e., the ortho-position relative to the nitro groups), due to the combination of induction effects, conjugation effects, and hydrogen bonds.[15] However, up to the present, the interactions in Case

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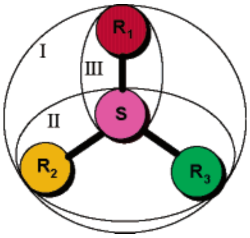


Figure 1. Chemical circumstance in $SR_1R_2R_3$. I denotes the whole molecule. II, III, and S denote the circumstances relative to R_1 group, the interaction between the R_2 and R_3 groups, and the interaction among the R_1, R_2, and R_3 groups, respectively.

III could only be qualitatively described. A quantitative method to calculate the IE is urgently needed for the purposes of comparison and evaluation.

I have two intentions in this paper: one is to establish a model to describe the interaction and introduce a method to calculate the corresponding IE for Case III; the other is to apply this method to investigate the correlation between the IE and stability of some nitro compounds, include nitro substitutes of methane, benzene, and cubane, due to their special requirement of safety as energetic materials.

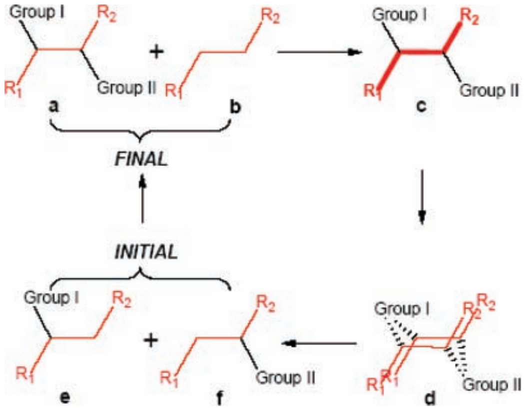
2. Theory and Computational Details

2.1. Model for Calculating IE Among Unlinked Groups or Atoms in One Molecule. Comparing Cases I and II with Case III in Scheme 1, we found that the key difference lies in the interacting manner. That is to say, the interactions are direct in the former two but indirect in the last one where amino and nitro groups are indirectly linked through a benzene ring. IEs of the former two cases can be obtained by directly dividing the relevant systems into two parts (i.e., two discussion objects) and calculating the energy changes. These can be described as IE $= E(M1\cdot\cdot\cdot M2) - E(M1) - E(M2)$ for Case I, and IE $= E(R1 - R2) - E(R1) - E(R2)$ for Case II. Different from Cases I and II, there is an "*additional object*" or a "*bridge*" in Case III, such as the benzene ring in nitroaniline, that connects the discussion objects (amino and nitro groups) together. Since people usually regard the residual parts of a system after the discussion objects have been removed as a so-called circumstance, we also consider the bridge as the circumstance influencing the interaction. From the viewpoint of chemistry, this circumstance could be structural or electronic and should be taken into account in calculating the IE among indirectly linked groups or atoms within one molecule.

Above all, the chemical circumstance of an interaction, such as the above-mentioned benzene ring, should be confirmed. Figure 1 illuminates a system and three circumstances depending on the different interested objects.

In Scheme 2, the interacting Groups I and II in molecule **a** are the investigation objects, and the so-called circumstance is **b**, which is the residual part of **a** after Groups I and II are removed. Molecule **c** is the superposition of **a** and **b**, similar to a complex. The overlapping part sketched in red and bold is the circumstance. Complex **c** dissociates via **d** to **e** and **f**. Consequently, the interaction between Groups I and II can be denoted as the reaction **e** + **f** (INITIAL) → **a** + **b** (FINAL), and the energy change is the IE. As is shown in Scheme 2, it is necessary to clarify the chemical structures before and after interactions before the calculation of IE. Because the structures after interactions (i.e., the investigation objects, such as **a**) are always known (the interested objects are the groups in a given molecule), the remaining work is to find the structures before interaction. As mentioned above, we must take into account the effect of the so-called circumstance on the interaction between indirectly linked groups, and the structure before interaction should contain the interested object and the circumstance. The simplest way to find the INITIAL structure is to combine the interested objects and the circumstance. For example, INITIAL **e** and **f** are just the circumstance **b** plus the unlinked Groups I and II, respectively. Comparing the structures of **e** and **f** with that of **a**, we find that all of them possess a common part, that is, chemical circumstances. Because the interacting circumstances remain similar in both INITIAL and FINAL structures, the influence of the circumstance on IE should be negligible. In other words, the IE of indirectly linked groups in one molecule can be defined as the energy difference after and before interaction while the groups are kept in similar circumstances. For example, in Scheme 2, molecules after and before interaction, **a**, **e**, and **f**, contain the same circumstance **b**. Because **e** + **f** has two **b**'s, one **b** needs to be added to **a** so that the equation **e** + **f** → **a** + **b** is balanced for IE calculating. Additionally, it should be noted that hydrogen atoms are used to saturate all the structures during the designing, for they are the smallest atoms and have the least effects on the chemical circumstance.

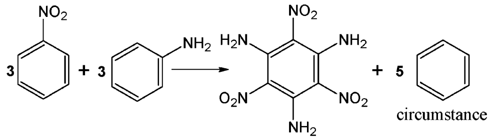
SCHEME 2. Model for Describing the Interaction between Unlinked Groups I and II



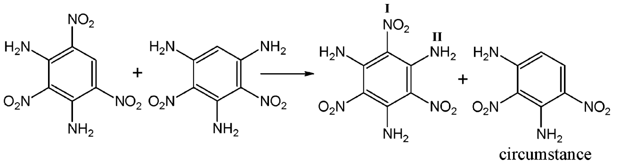
Overall, the process of designing reactions to calculate the IE of indirectly linked groups or atoms in one molecule can be summarized as follows: (1) determine the interacting groups such as Groups I and II in Scheme 2; (2) remove the interacting groups from the molecule regarded as a system, and obtain the circumstance molecule such as **b**; use the interested molecule and the circumstance to compose the FINAL; (3) obtain the new molecules containing the circumstance with individual object groups (**e** and **f**), and use them to compose the INITIAL; and (4) calculate the IE using eq 1. Seemingly, this process is similar to designing an isodesmic reaction, and the corresponding IE is the energy change of the reaction. However, the process is not completely equivalent to an isodesmic reaction design because there may be many isodesmic reactions for an object molecule, but only one of them is capable of describing a given interaction.

Four designed reactions are presented in Scheme 3 to illustrate four kinds of interactions in TATB, including ALL, MON−MON, MON−POLY and POLY−POLY, and to clarify the process and the chemical meaning of IE. Although the TATB molecules are the same in the four processes, different isodesmic reactions represent different interactions. That is, there is only one reaction corresponding to a given interaction. Focusing on

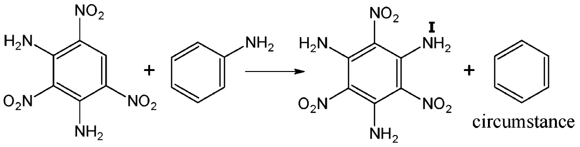
SCHEME 3. Four Kinds of Interactions among Indirectly Linked Groups in TATB



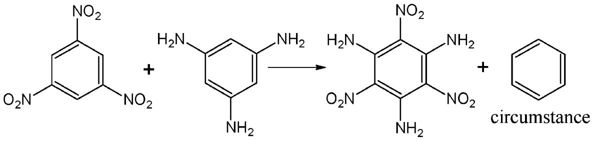
Interaction among the all amino and nitro groups (ALL)



Interaction between nitro group(I) and amino group(II) (MON-MON)

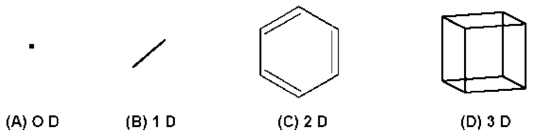


Interaction between amino group I and all other groups (MON-POLY)



Interaction between three amino groups and three nitro groups (POLY-POLY)

SCHEME 4. Molecular Nuclear Parts of Different Dimensionalities



the molecular stabilities, we will only discuss the interaction among all substituted groups, that is, only the ALL case in this paper.

Therefore, from the above discussion, an equation for calculating the IE between two substituted groups within one molecule can be obtained as eq 2:

$$\mathrm{IE} = E_{\mathrm{object}} + E_0 - (E_1 + E_2) \tag{2}$$

Similarly, a common equation for calculating IE among n ($n \geq 2$) groups can be written as

$$\mathrm{IE} = E_{\mathrm{object}} + (n-1)E_0 - \sum_{i=1}^{n} E_i \tag{3}$$

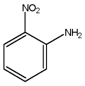
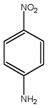
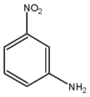
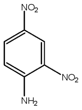
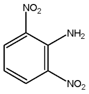
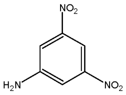
In above two equations, E_{object}, E_0, and E_i (E_1, E_2, ...) are the total energies of the object molecules with all the interested groups, molecules without any interested group, and molecules with only one interested group, respectively. Certainly, all molecules have the same "nuclear parts" On these nuclear parts, substituted groups and hydrogen atoms are added to compose the closely related molecules. For example, A, C, and D in Scheme 4 respectively represent the nuclear parts of nitro substitutes of methane, benzene, and cubane, possessing different dimensionalities. It should be noted that (1) the IE is the energy change of a special and unique isodesmic reaction; (2) the IE is a value relative to the IE of hydrogen atoms whose absolute value is unknown; namely, the IE of hydrogen atoms is defined as zero; (3) only for separate groups of closely related molecules is it meaningful to discuss the IE due to above reason; and (4) in this case, the IE is not a real IE in the traditional sense of the term. Instead, it reflects a comprehensive effect of interacting groups within one molecule. In particular, the IE of all substituted groups reflects quantitatively the change in the combinative strength of these groups and the encompassed nuclear parts. This point will be discussed in section 3.2.

2.2. Methods of Comparing and Evaluating the Molecular Stabilities of Nitro Compounds. Now, people pay more attention to the security of armament including explosives. The relationship between the sensitivity (stability) and the molecular structure of high energy density materials has become an important subject. The "trigger linkage" is a popular and important concept in which a bond break is the key step in detonation initiation. Many researchers believe that C−nitro, N−nitro, and O−nitro bonds are trigger spots in nitro explosives. Depluech and Cherville proposed that shock wave and thermal sensitivities in nitro compounds could be related to the electronic structure of the molecule and properties of C−nitro, N−nitro and O−nitro bonds, such as electrostatic potentials, lengths, strengths, and so forth.[17−19] Xiao suggested that the stronger these bonds are, the more stable the molecules become.[20] Bates pointed out that the sensitivity of tetrazole is proportional to the electron-attraction ability of substitution groups.[21] Kamlet and Adolph concluded that the impact sensitivities of some nitro compounds increase when their oxygen balances are enhanced.[22] Politzer thought that sensitivity must depend on the electrostatic potential on the molecular surface, and more details were presented in his paper.[23] Zeman's work is notable 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.[24] Rice et al. correlated the impact sensitivities and dissociation energies of C−nitro bonds (BDE) of nitrobenzene explosives.[12] Our recent work provided another way to assess the molecular stabilities of some nitro compounds by computing the electron-attracting ability of nitro groups denoted by τ, which is the sum of the Mulliken populations of the nitro groups. The larger the τ was, the less sensitive the compound would be.[25] We also found a correlation between the impact sensitivities and the nitro group charges in nitro explosives.[26] In this paper, the molecular stabilities will be assessed and compared with the existing C−nitro bond length ($R_{\mathrm{C-nitro}}$), nitro group charges (Q_{nitro}), oxygen balance (OB), BDE, impact sensitivity measured by the drop height H_{50}, and the above-mentioned IE among all substituted groups.

2.3. Computational Details. Nowadays, density functional theory (DFT) methods,[27,28] particularly the B3LYP[29,30] hybrid DFT method, have been widely employed to deal with complex and electron correlation problems because they not only produce reliable geometries and energies but also require less time and computer resources. In all our quantum mechanics calculations, we also use the BLYP hybrid DFT method with the DNP (double numeral adding polarization) basis set in Dmol^3,[31−33] similar to 6-31G** in Gaussian. All stable optimized structures were confirmed by no imaginary frequency.

According to the above-mentioned calculation method of the IE of all substituted groups in one molecule, three general isodesmic reactions are designed as illustrated below, corresponding to the nitro substitutes of methane, benzene, and cubane, respectively. The variables m and n in the reactions denote the numbers of nitro groups and amino groups, respec-

TABLE 1. Calculated IEs of Nitroanilines and Dinitroanilines

Compound						
IE, kJ/mol	-17.68	-14.24	-4.95	-15.75	-15.46	6.91

tively. IEs are the energy changes caused by the reactions.

$$mCH_3NO_2 \rightarrow CH_{4-m}(NO_2)_m + (m-1)CH_4$$

$$mC_6H_5NO_2 + nC_6H_5NH_2 \rightarrow C_6H_{6-m-n}(NO_2)_m(NH_2)_n + (m+n-1)C_6H_6$$

$$mC_8H_7NO_2 \rightarrow CH_{8-m}(NO_2)_m + (m-1)C_8H_8$$

Finally, the oxygen balance (based on the oxidation product of carbon, CO_2) of a nitro compound $C_aH_bO_cN_d$ was redefined as eq 4. The nitro group charges (Q_{nitro}) were calculated using eq 5, where Q_N, Q_{O1} and Q_{O2} were the charges of the N and O atoms on the nitro group, respectively.[26] Also, the average nitro group charges ($\bar{Q}_{\mathrm{nitro}}$) were defined as eq 6. According to Politzer's suggestion,[23] the largest molecular electrostatic potentials ($V_{\mathrm{mid,max}}$) were introduced as eq 7, where Q_R is the charges of C, N, or O atoms linked with the nitro group, $Q_{\mathrm{N(nitro)}}$ is the charges of the N atom on the nitro group, and $R_{R-\mathrm{nitro}}$ is the R−nitro bond length.

$$OB(CO_2) = \frac{c - (2a + b/2)}{2a + b/2} \times 100\% \qquad (4)$$

$$Q_{\mathrm{nitro}} = Q_N + Q_{O1} + Q_{O2} \qquad (5)$$

$$\bar{Q}_{\mathrm{nitro}} = \frac{1}{n}\sum_{i=1}^{n} Q_{\mathrm{nitro},i} \qquad (6)$$

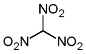
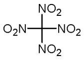
$$V_{\mathrm{mid,max}} = \frac{2(Q_R + Q_{\mathrm{N(nitro)}})}{R_{R-\mathrm{nitro}}} \qquad (7)$$

3. Results and Discussion

Before discussing the correlation between the IE and molecular stability of three groups of nitro compounds, we listed the IE of two groups of isomers, nitroanilines and dinitroanilines, in Table 1. For any group of isomers, because the INITIALs in isodesmic reactions are the same, the isomer with lower total energy corresponding to the better molecular stability gives lower IE. It verifies that IE is consistent with the stability, and the model presented in the paper is reliable. Organic chemistry theory has already qualitatively explained the interactions among the substituted groups on different positions, which are attributed to induction effects, conjugation effects, and hydrogen bonds. IE provides quantitative data showing the difference of these interactions.

3.1. Nitro Substitutes of Methane. IE and four other indexes were used to evaluate the stabilities of nitro substitutes of methane, which are usually taken as the simplest samples of nitro compounds. From Table 2, we can see that five indexes can well explain the reason why the substitution of hydrogen atoms by nitro groups caused the decrease in stability: (1) nitro group charges Q_{nitro} indicate that the substitution causes the less and less negative charges on the nitro group when hydrogen atoms (electron-donors) are replaced by nitro groups (electron-acceptors); (2) C−nitro bond lengths $R_{\mathrm{C-nitro}}$ are lengthened as a result of the repulsion of the nitro groups; (3) molecular electrostatic potential V_{mid} becomes more positive, and the increases in the positive charges on carbon and nitrogen atoms are faster than $R_{\mathrm{C-nitro}}$; (4) OB increases with the increase of nitro groups and the decrease of hydrogen atoms, as nitro groups possess positive oxygen balances and hydrogen atoms possess negative oxygen balances; (5) the IEs of all unlinked nitro groups rise, indicating an increase in repulsion. Here we find that IE can be used as a tool to assess the molecular stability. That is, for a group of analogues, the more positive IE corresponds to worse stability, and vice versa.

TABLE 2. Calculated Results of Nitro Substitutes of Methane

compound	H_3C-NO_2			
Q_{nitro} (e)	−0.285	−0.192	−0.152	−0.050
$R_{\mathrm{C-nitro}}$ (Å)	1.517	1.543	1.548	1.582
$V_{\mathrm{mid,max}}$	0.123	0.185	0.227	0.244
$OB(CO_2)$ (%)	−42.87	33.33	140.00	300.00
IE (kJ/mol)		43.5	115.5	202.3

3.2. Nitro and Amino Substitutes of Benzene. The nitrobenzenes shown in Figure 2 contain at least three nitro groups. They are typical nitro explosives for a structure−impact sensitivity relationship investigation. Their impact sensitivities have been evaluated by molecular electrostatic potentials, bond length, bond orders, BDEs, energy gaps between the highest occupied molecular orbital (HOMO) and the lowest unoccupied orbital (LUMO), electron-attraction abilities of substitution groups, oxygen balances, and nitro group charges.[17−27] Here we use them to study the IE−impact sensitivity correlation. There are many factors influencing the impact sensitivities of explosives; however, the molecular stability is the crucial one. It is necessary to calculate IE for the investigation of molecular stabilities and the IE−impact sensitivity relationship of these explosives, as has been done with the lowest BDE of the C−nitro bond in the molecule (BDE), the nitro group charges including the minimum ($Q_{\mathrm{nitro,min}}$) and the average ($\bar{Q}_{\mathrm{nitro}}$), the longest C−nitro bond length ($R_{\mathrm{C-nitro,max}}$), and oxygen balances (OB). All results in Table 3 were calculated using the methods introduced in section 2 and plotted against H_{50} in Figure 3. From HNB to TATB, with the decrease in nitro groups and the increase in amino groups, the stabilities of nitro explosives improve as indicated by the rising of H_{50}. In Figure 3, there are obvious correlations between these indexes and H_{50}. Particularly, the correlations related to oxygen balances and IE have the best monotonicity. For these analogues, the more negative IE means the stronger attraction among these substituted groups and the better stabilities of molecules.

All the noncomplete monotonicity occurs when the number of substituted nitro groups exceeds three. The compounds containing at least four nitro groups, such as HNB, PNB, PNA, TETNB, and TETNA, are usually unstable due to the strong repulsions among the nitro groups. It could be ascribed to the structural complexity of these molecules that the changes of

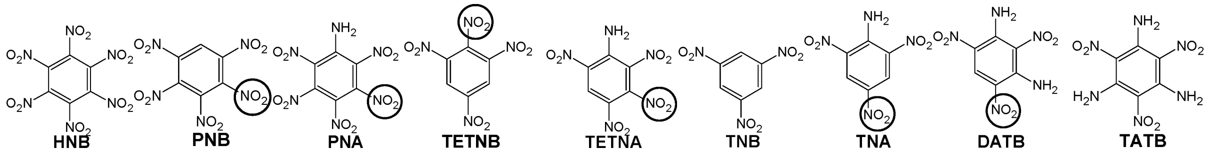


Figure 2. Nitrobenzene explosives containing at least three nitro groups. The nitro groups indicated in circles have $Q_{\text{nitro,min}}$, $R_{\text{C-nitro,max}}$, and the lowest BDE in the molecule.

TABLE 3. Calculated Results of Nitro Substitutes of Benzene

compound	HNB	PNB	PNA	TETNB	TETNA	TNB	TNA	DATB	TATB
H_{50} (m)	0.12		0.15	0.27	0.41	1.00	1.77	3.20	4.90
BDE[a] (kJ/mol)	209.5	195.8	197.0	210.4	201.2	267.6	278.1	289.4	290.2
ΣΔBDE[b] (kJ/mol)	−511.6	−339.3	−324.7	−218.5	−123.7	−59.4	−5.9	98.1	123.6
$Q_{\text{nitro,min}}$ (e)	−0.161	−0.156	−0.163	−0.160	−0.165	−0.228	−0.289	−0.355	−0.442
Q_{nitro} (e)	−0.161	−0.183	−0.216	−0.211	−0.252	−0.251	−0.311	−0.376	−0.442
$R_{\text{C-nitro,max}}$ (Å)	1.510	1.509	1.514	1.506	1.511	1.502	1.483	1.469	1.446
OB(CO_2) (%)	0.0	−20.0	−23.1	−38.5	−40.7	−55.6	−57.1	−58.6	−60.0
IE (kJ/mol)	354.43	253.57	220.65	150.89	111.86	48.46	5.15	−33.22	−53.74

[a] The BDE values of nitrobenzenes except from PNB are cited from ref 12. [b] ΣΔBDE = ΣΔBDE(C−NO_2) + ΣΔBDE(C−NH_2). ΔBDE is the BDE difference between nitro explosive molecules and nitrobenzene or aniline. For example, BDE(C−NO_2) and BDE(C−NH_2) of Ph−NO_2, Ph−NH_2, and TATB are 229.0, 355.8, and 250.6, and 375.4 kJ/mol, respectively. So, for TATB, ΣΔBDE = ΣΔBDE(C−NO_2) + ΣΔBDE(C−NH_2) = 3*(250.6−229.0) + 3*(375.4−355.8) = 123.6 kJ/mol. BDE is calculated at the PM3/UHF level using the VAMP module in Material Studio 3.0.[33]

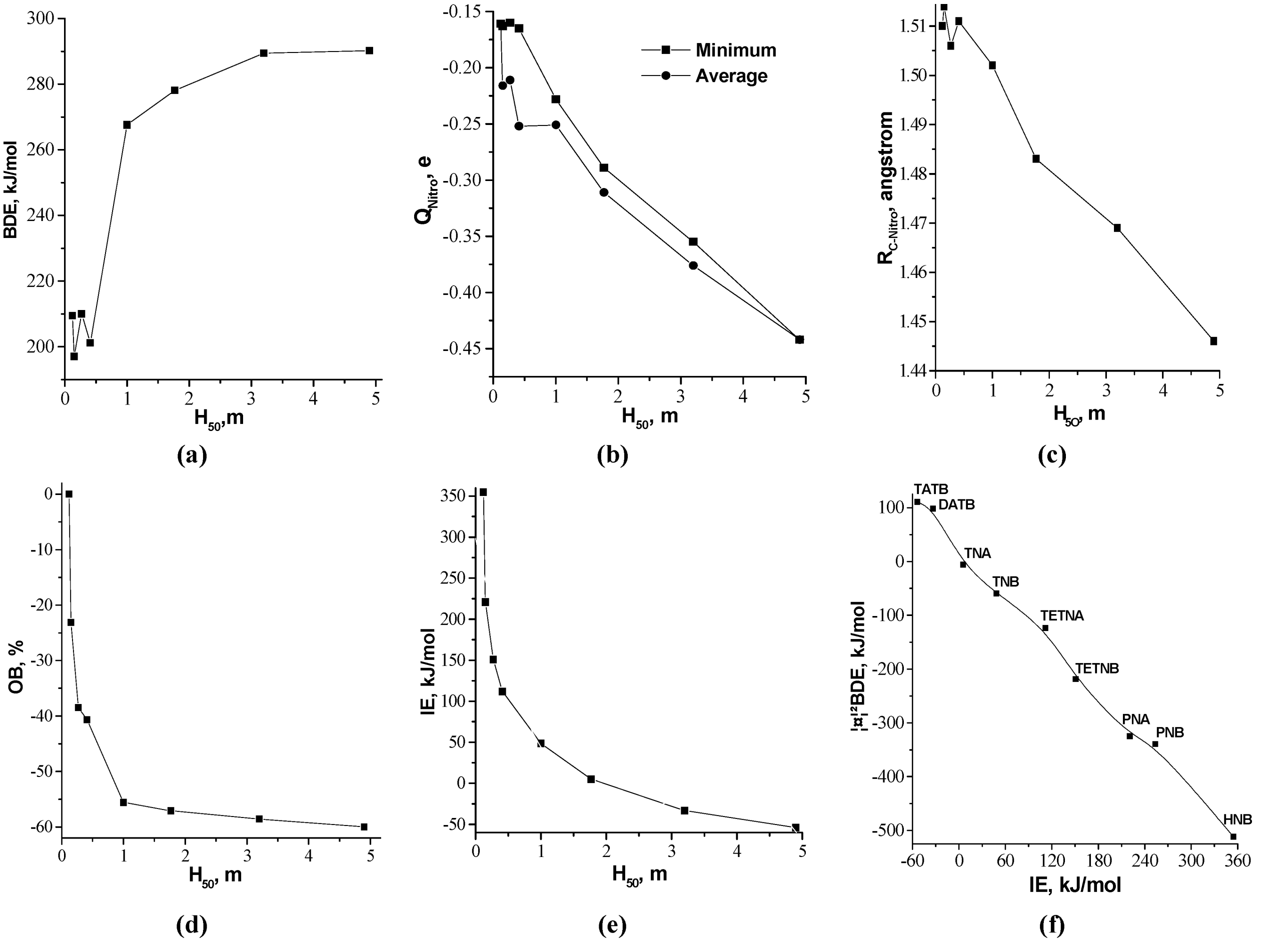


Figure 3. Correlations of impact sensitivity (H_{50}) and C−nitro BDE (a), nitro group charges (b), C−nitro bond length (c), oxygen balance (d), and IE of all substituted groups (e), as well as the correlation of IE and ΣΔBDE (f) of nitrobenzene explosives.

BDE, Q_{nitro} and $R_{\text{C-nitro}}$ are not monotonously. Some unexpected indexes of good stability of HNB may be attributed to its high symmetry. The longer C−nitro bonds of unstable PNA and TETNA could be considered the result of the mesomeric effect of amino groups on the meta-position relative to nitro groups.

Because BDE is an important and commonly used parameter to evaluate the molecular stability, it should be helpful to discuss the IE−BDE relationship. Panels a and e in Figure 3 imply that there is no complete monotonic trend of IE versus BDE. However, according to the definition of IE, IE reflects the change of the combinative strength of the amino and nitro

TABLE 4. Calculated Results of Nitro Substitutes of Cubane[a]

n	$Q_{\text{nitro,min}}$ (e)	$\bar{Q}_{\text{nitro}}$ (e)	IE (kJ/mol)	OB(CO_2) (%)
1	−0.316(1)	−0.316	0	−84.0
2	−0.276 (12), −0.289(13), −0.295(14) −0.286*	−0.276, −0.289, −0.295 −0.286*	26.03, 16.01, 13.27 19.65*	−69.2
3	−0.237(123), −0.249(127), −0.265(137) −0.251*	−0.249, −0.260, −0.265 −0.257*	64.96, 52.94, 44.60 54.78*	−55.6
4	−0.219(1236), −0.220(1238), −0.224(1237) −0.245(1235), −0.274(1267), −0.281(1357) −0.250*	−0.231, −0.220, −0.235 −0.264, −0.276, −0.284 −0.252*	165.49, 181.40, 151.26 127.05, 111.33, 102.76 134.13*	−42.9
5	−0.228(12378), −0.228(12357), −0.238(12678) −0.233*	−0.243, −0.248, −0.252 −0.248*	241.57, 223.24, 226.44 232.41*	−31.0
6	−0.179(123678), −0.179(123578), −0.192(134567) −0.186*	−0.185, −0.189, −0.193 −0.189*	257.88, 246.53, 241.01 249.35*7	−20.0
	−0.164(1234567)	−0.168	338.34−9.7	
8	−0.149(12345678)	−0.149	433.22	0.0

[a] Note: *n* is the number of nitro groups in the substitutes. * denotes the average of the maximum and minimum in its above cell lattice. The number in brackets denotes the linking position of the nitro group.

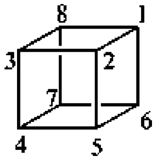


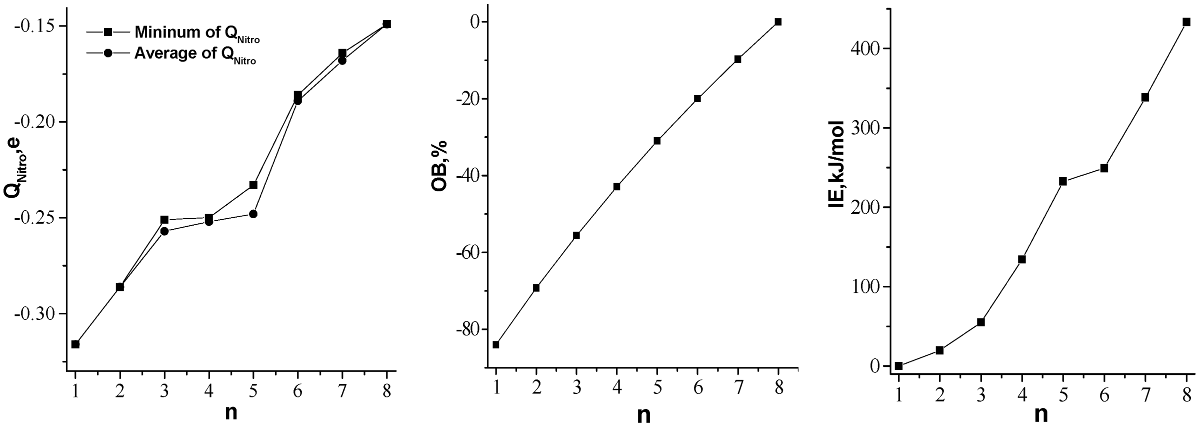
Figure 4. Molecular framework and atomic numbering of cubane.

groups and the benzene ring (nuclear part), which can be assessed by BDE changes, ΣΔBDE. Therefore, a monotonic trend of IE−ΣΔBDE can be found in Figure 3f, confirming the physical meaning of IE induced by the interaction among all substituted groups and reflects the molecular stability. Namely, the more negative IE or positive ΣΔBDE, the more stable the molecule. IE and BDE are sometimes inconsistent with each other because IE represents the comprehensive effects of all substituted groups and agrees with ΣΔBDE, but BDE represents the individual effect of an appointed bond. For instance, among HNB, PNB, PNA, and TETNA, HNB has the largest BDE and the strongest C−nitro bond but the most positive IE and the most negative ΣΔBDE. This inconsistency is attributed to the different quantities of C−nitro and/or C−amino bonds and their different BDE changes. On the contrary, TATB has the largest ΔBDE and the most quantities of C−nitro and/or C−amino bonds out of TNB, TNA, DATB and TATB. So it has the largest ΣΔBDE corresponding to the most negative IE and the most molecular stability. In this case, BDE has agreement with IE.

Additionally, for this group of analogues (as in Figure 3b), the nitro group charges denoted by the average nitro group charges are not better than those denoted by the minimal nitro group charges for describing the $Q_{\text{nitro}}-H_{50}$ correlation. According to the calculation, the nitro group having the least negative charges often corresponds to the longest C−nitro bond length and the lowest C−nitro BDE. In other words, the value of nitro group charges can reflect the strength of the corresponding bond, particularly in multi-nitro molecules.

Again, impact sensitivities are well related with OB and IE, as shown by the two monotonic curves d and e in Figure 3. From HNB, PNA, TETNB, TETNA, TNB and TNA, to DATB and TATB, their IEs decrease from positive values that mean repulsion and bad stability (354.43, 220.65, 150.89, 111.86, 48.46, and 5.15 kJ/mol) to negative values that mean attraction and good stability (−33.22 and −53.74 kJ/mol); in the mean time, the impact sensitivities measured by H_{50} increase from 0.12 m to 0.15, 0.27, 0.41, 1.00, 1.77, 3.20, and 4.90 m, respectively. The consistence of IEs and impact sensitivities confirm that IE is a good tool to evaluate the molecular stability. The more positive IE results in an unstable compound, whereas the more negative IE results in a stable one. Consequently, it may be an efficient way to enhance the molecular stability by increasing its negative IE. For example, to introduce three amino groups into TNB to form TATB, the most famously insensitive and the so-called wood explosive, can distinctly increase negative IE.

3.3. Nitro Substitutes of Cubane. Prior to 2000, all nitro substitutes of cubane were synthesized.[34,35] Among these substitutes, octanitrocubane (ONC) possesses a cage-shaped



(a) (b) (c)

Figure 5. Correlation of nitro group charges (a), oxygen balance (b), and the IE of all nitro groups (c), and the number of substituted nitro groups of nitrocubanes. The nitro group charges and interaction energies of isomers are treated by their averages.

structure and a zero oxygen balance, resulting in very high crystal density, very high detonation heat, and very good detonation properties, and seems to be a potential important energetic material. However, it has a fatal disadvantage, that is, the bad stability. So far, 6 years after ONC was synthesized, there has been no report on its application. In Table 4, the IEs of all nitro groups, nitro group charges, and oxygen balances were calculated to evaluate the molecular stability. There are 21 nitro substitutes of cubane. When the number of nitro groups reaches 2, 3, 4, 5, or 6, there exist isomers. For any group of isomers, oxygen balance is no longer a useful tool, as they are same for the same chemical component. Although the rule of oxygen balance is convenient to consider only chemical components, it is also limited without considering chemical structures. However, nitro group charges and IEs can distinguish the stability differences of these isomers.

In Figure 5 the curves correlating stability indexes versus the number of nitro groups (*n*) converted from Table 3 can well reflect the stability changes. That is to say, the increase of nitro groups can result in the decrease of the negative nitro group charges, the increase of the oxygen balances, and the increase of the positive IEs corresponding to repulsion and instability. This is the case described in section 3.1.

Conclusion

For the first time, a model of IE is introduced in this paper for calculating the IE of indirectly linked groups or atoms within one molecule, and applied to three cases including nitro substitutes of methane, benzene, and cubane. All results show that the IE of all substituted groups is a new, quantitative, and useful tool to evaluate the stabilities of nitro compounds. Also, according to these investigation objects, it should be pointed out that its overall significance is limited by the fact that it is applied only to separate groups of closely related molecules.

Acknowledgment. I greatly appreciate the financial support from CAEP's funds (No. 626010910). Also, I thank Mr. Liu Jian, Institute of Applied Computer, CAEP, very much for his help on computation, and Dr. Wei Zhong, Institute of Chemical Materials, CAEP, for his suggestions on English expressions.

References and Notes

(1) Hobza, P.; Šponer, J. *Chem. Rev.* **1999**, *99*, 3247.

(2) Dorescu, D. C.; Boatz, J. A.; Thompson, D. L. *J. Phys. Chem. B.* **2003**, *107*, 8953.

(3) Dorescu, D. C.; Boatz, J. A.; Thompson, D. L. *J. Phys. Chem. B.* **2005**, *109*, 1451.

(4) Ju, X. H.; Li, Y. M.; Xiao, H. M. *J. Phys. Chem. A.* **2005**, *109*, 934.

(5) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(6) Gianinetti, E.; Raimondi, M.; Tornaghi, E. *Int. J. Quantum. Chem.* **1996**, *60*, 157.

(7) Simon, S.; Duran, M.; Dannenberg, J. J. *J. Chem. Phys.* **2000**, *113*, 5666.

(8) Paizs, B.; Salbador, P.; Császár, A. G.; Duran, M.; Sohai, S. *J. Comput. Chem.* **2001**, *22*, 196.

(9) Head-Gordon, M.; Head-Gordon, T. *Chem. Phys. Lett.* **1994**, *220*, 122.

(10) Saebo, S.; Almlof, J. *Chem. Phys. Lett.* **1989**, *154*, 83.

(11) Trucks, G. W.; Watts, J. D.; Salter, E. A.; Bartlett, R. J. *Chem. Phys. Lett.* **1988**, *153*, 490.

(12) Rice, B. M.; Sahu, S.; Owens, F. J. *J. Mol. Struct. (THEOCHEM)*, **2002**, *583*, 69.

(13) Hrovat, D. A.; Borden, W. T.; Eaton, P. E. *J. Am. Chem. Soc.* **2001**, *123*, 1289.

(14) Zhang, C.; Shu, Y.; Huang, Y.; Zhao, X.; Dong. H. *J. Phys. Chem. B* **2005**, *109*, 8978.

(15) Zhang, C. *Chem. Phys.* **2006**, *324*, 547.

(16) Dong, H.; Zhou, F. *Properties of High Energetic Explosives and Relatives*; Science Press: Beijing, 1989.

(17) Delpuech, A.; Cherville, J. *Proc. 1st Symp. Chem. Probl. Connected Stab. Explos.* **1976**, 298.

(18) Delpuech, A.; Cherville, J. *Propellants Explos.* **1978**, *3* (6), 169.

(19) Delpuech, A.; Cherville, J. *Propellants Explos.* **1979**, *4* (6), 121.

(20) Heming, X. *Molecular Orbital Theory of Nitro-compound*; Publishing House of Defense Industry: Peking, China, 1994 (in Chinese).

(21) Bates, L. R. *Proc. 13th Symp. Explos. Pyrotech.* **1986**, 251.

(22) Kamlet, M. J.; Adolph, H. G. *Propellants Explos.* **1979**, *4* (2), 30.

(23) Owens, F. J.; Jayasuriya, K.; Abrahmsen, L.; Politzer, P. *Chem. Phys. Lett.* **1985**, *116*, 434. Murray, J. S.; Lane, P.; Politzer, P.; Bulduc, P. R. *Chem. Phys. Lett.* **1990**, *168*, 135.

(24) Zeman, S. In *Energetic Materials, Part 2*; Politzer, P., Murray, J. S., Eds.; Elsevier: Amsterdam, 2003; pp 25−52.

(25) Zhang, C.; Shu, Y.; Huang, Y.; Zhao, X.; Wang, X.; Dong, H. *Sci. Tech. Energ. Mater.* **2004**, *65* (6), 191.

(26) Zhang, C.; Shu, Y.; Wang, X.; Zhao, X.; Tan, B.; Peng, R. *J. Phys. Chem. A* **2005**, *109*, 6592.

(27) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, 1989.

(28) Seminario, J. M.; Politzer, P. *Modern Density Functional Theory: A Tool for Chemistry*; Elsevier: Amsterdam, 1995.

(29) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(30) Becke, A. D. *J. Chem. Phys.* **1992**, *97*, 9173.

(31) Delley, B. *J. Chem. Phys.* **1990**, *92*, 508.

(32) Delley, B. *J. Chem. Phys.* **2000**, *113*, 7756.

(33) *Material Studio 3.0*; Accelrys, Inc.: San Diego, CA, 2003.

(34) Schmitt, R. J.; Bottaro, J. C. U.S. Patent AD-A263271, 1993.

(35) Zhang, M. X.; Eaton, P. E.; Gilardi, R. *Angew. Chem., Int. Ed.* **2000**, *39*, 401.