Received: 20 November 2007, Revised: 23 February 2008, Accepted: 1 March 2008, Published online in Wiley InterScience: 2008

(www.interscience.wiley.com) DOI 10.1002/poc.1369

Quantitative approach to evaluate the intramolecular interaction of the appointed and unlinked groups or nonhydrogen atoms within organic compounds

Chaoyang Zhang[a*]

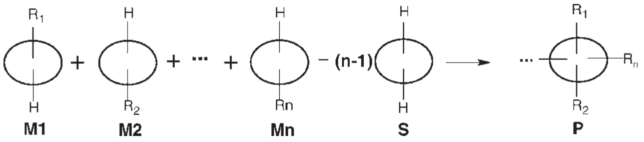
This paper reported a new approach to quantitatively evaluate the interaction of the appointed and indirectly linked groups or nonhydrogen atoms in molecules by designing unique isodesmic reactions, calculating their energy changes, and getting so-called interaction energy (E_i). The consistency of the sign and amount of E_i with the common qualitative descriptions on some intramolecular effects confirmed the validity of the new method. Two applications of this method to halogenated methane and ethane, and nitro compounds showed: (1) for any group of molecules with the same skeleton, E_i of all substitution groups or nonhydrogen atoms can be used to compare their molecular stabilities; (2) for the appointed groups in different molecules, E_i of them can reveal the nature (attraction or repulsion) and the strength of their interaction. All these indicated that E_i is a useful tool to reflect the intramolecular interaction of appointed and unlinked groups or nonhydrogen atoms. Copyright © 2008 John Wiley & Sons, Ltd.

Supplementary electronic material for this paper is available in Wiley InterScience at http://www.mrw.interscience.wiley.com/suppmat/0894-3230/suppmat/

Keywords: intramolecular effect; interaction energy; organic compounds

INTRODUCTION AND METHODOLOGY

Organic compounds are a sort of ones in which the interactions among substitution groups are stressed.[1–8] The interaction energy between two substitution groups (SIE) was proposed and defined as the energy change of a unique isodesmic reaction by Guo *et al*. to well interpret the Pauling electronegativity and Hammett equation.[9] On the basis of their finding, they hypothesized that the electronic substituent effect in a multi-substituted system (SIE) should follow a simple equation involving a constant dependent on the system and a certain scale of electronic substituent constant. The equation is applicable to many organic systems such as disubstituted bicyclo[2.2.2]octanes, benzenes, ethylenes, butadienes, and hexatrienes. Here, we highlight the substitutent effect on the molecular stability. When a group of molecules possess a same molecular skeleton, the difference of their stabilities should be determined by these effects. For example, in Scheme 1, nitromethane becomes weaker and weaker with the increasing repulsion among nitro groups, as well as nitroethane, nitrobenzene and nitrocubane. Usually, the qualitative descriptions of these interactions according to the common organic theory can well explain some intramolecular effects. However, sometimes, the quantitative descriptions are necessary when qualitative ones are inefficient. For instance, it may be difficult to compare the interactions among nitro and amino groups in benzene derivatives in Scheme 2 by qualitative descriptions. Reference [10] just proposed a quantitative description of these interactions among the indirectly linked groups or nonhydrogen atoms within a molecule and applied it to evaluate molecular stabilities. This approach can be summarized as two common equations 1 and 2, which denote a unique isodesmic reaction and its energy change, respectively, and where E_i is the interaction energy of unlinked groups R_1, R_2, . . ., and R_n in molecule *P*.



(1)

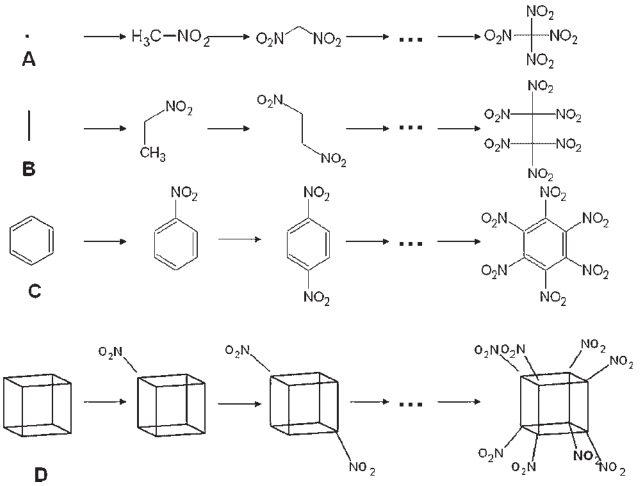
$$E_i = E(P) + (n-1)E(S) - \sum_{i=1}^{n} E(M_i) \qquad (2)$$

The similarity of the compounds M1, M2, . . ., Mn, *S* and *P* in Eqn (1) makes the method applicable to a group of molecules with the same skeleton under a comprehensive consideration (E_i is of all substitution groups or atoms). As a matter of fact, people usually evaluate and predict molecular stabilities according to

---

* Laboratory of Material Chemistry, Institute of Chemical Materials, China Academy of Engineering Physics (CAEP), P. O. Box 919-327#, Mianyang, Sichuan 621900, P R China.
E-mail: zcy19710915@yahoo.com.cn

a C. Zhang
Laboratory of Material Chemistry, Institute of Chemical Materials, China Academy of Engineering Physics (CAEP), Mianyang, Sichuan, P R China



Scheme 1. Qualitative theory is enough to describe the repulsion among nitro groups in compounds

their sorts. These cases may most occur in the field of energetic materials. Molecular skeletons are kept invariable with changing substitution groups to satisfy different requirements. For example, by changing the amount and site of nitro or amino groups in the derivatives of benzene, people can get the energetic materials with different performance such as density, sensitivity, detonation, and so forth. The stabilities of a group of molecules with same skeleton can be compared by the interaction of all substitution groups. Experimental evidences have showed there a big difference of thermal stability related with molecular stability among the amino-nitro derivatives of benzene in Scheme 2—the weakest HNB has close 200 °C DSC decomposition temperature far lower than that of the most stable TATB, above 370 °C. And other molecules have the thermal stabilities between them.[11] This phenomenon can be readily interpreted by the new method. That is to say, HNB has the largest E_i 354 kJ/mol (in Table 1) implying the most repulsion among all six nitro groups and the lowest molecular stability; whereas TATB has the least E_i -54 kJ/mol implying the most attraction among the three nitro groups and three amino groups and the highest molecular stability. Based on the previous work, this paper first confirmed the validity of the method by applying it to explore intramolecular effects and comparing their quantitative results with common qualitative descriptions, and further used it to discuss the molecular stabilities of halogenated methane and ethane. Furthermore, to be more important, by this method, the interaction of the appointed groups in different compounds was discussed in this paper. On the basis of these two points, it is time to establish the new method to employ E_i to reflect the nature and the strength of appointed groups or nonhydrogen atoms.

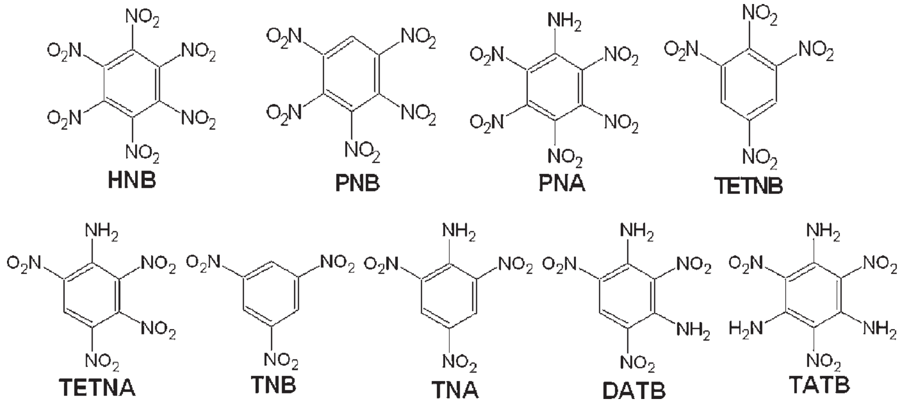
In all our quantum mechanics calculations, DFT/BLYP method with DNP (double numeral adding polarization) basis set in Dmol,[2,12–14] similar to 6–31G** in Gaussian, was employed. All stable optimized structures were confirmed by no imaginary frequency. Much practice confirmed that these methods are enough to calculate the single gas molecules contained in the paper.

RESULTS AND DISCUSSION

Validity confirmation of the new method

Nitro compounds, especially nitro explosives, are a group of important organic compounds due to their applications in many fields such as propellants, explosives, pyrotechnics, and so forth. We have some researches on their structure–property relationships previously.[15–17] Therefore, we selected these familiar nitro compounds as samples to discuss some effects in organic chemistry and confirm the validity of the new method. Certainly, this confirmation is based on the consistency of quantitative results and qualitative descriptions.

Before confirming the validity of the new method, we listed the interaction energy of two groups of isomers, dinitrobenzene and

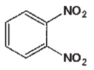
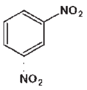
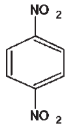
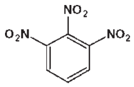
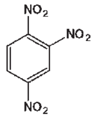
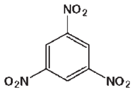


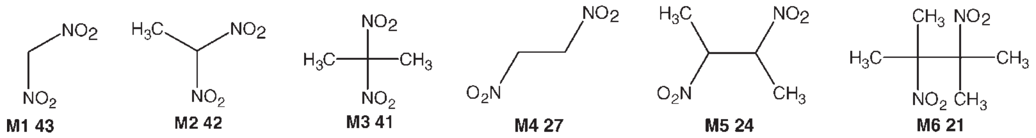
Scheme 2. Qualitative theory is inefficient to describe the interaction among amino and nitro groups in compounds and a quantitative method is necessary

Table 1. Calculated interaction energy of amino and nitro groups in the benzene derivatives cited from Reference [1]0

Compound	HNB	PNB	PNA	TETNB	TETNA	TNB	TNA	DATB	TATB
E_i, kJ/mol	354	254	221	151	112	48	5	−33	−54

Table 2. Two groups of isomers I1 and I2, and interaction energy E_i (unit in kJ/mol) among nitro groups in molecules

I1			I2		
 58	 17	 17	 114	 86	 48



Scheme 3. E_i (unit in kJ/mol) between two nitro groups influenced by the spatial steric effect of methyls

trinitrobenzene in Table 2. For any group of isomers, because the isodesmic reactions are same, the isomer with lower total energy corresponding to the better molecular stability gives lower E_i. It verifies that E_i is consistent with the molecular stability, and the method presented in the paper is reliable. Organic chemistry theory has already qualitatively explained the interactions among the substitution groups on different positions, which are usually attributed to induction effects, conjugation effects and hydrogen bonds. The quantitative data of E_i can also show the difference of these interactions.

Steric effect

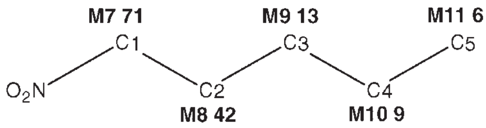
Interaction energy between nitro groups in simple dinitro alkanes is taken as the investigation objects here. By means of above method and Eqns 1 and 2, E_i between two nitro groups in different compounds were obtained in Scheme 3. As illustrated in the scheme, the increasing steric effect of methyls results in the decreasing interaction (repulsion) between two nitro groups. According to the data of E_i in the scheme, the appointed steric effect can be quantitatively described as: 1(43–42) kJ/mol of one methyl in M2; 2 (43–41) kJ/mol of two methyls in M3, 3 (27–24) kJ/mol of two methyls in M5, and 6 (27–21) kJ/mol of four methyls in M6. These quantitative descriptions agree well with the common sense of the steric effects in organic compounds.

Induction effect

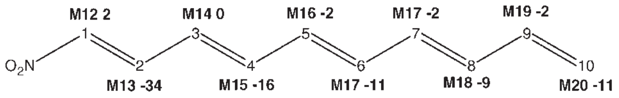
E_i between two nitro groups in dinitro pentane can well reflect the obvious induction effect as showed in Scheme 4. The quantitative result is in good agreement with the common qualitative description of induction effect: by increasing the distance between two nitro groups, the induction effect, that is the repulsion, between them decreases apparently from 71 to 42, 13, 9, and 6 kJ/mol. When two nitro groups part from a distance of three carbon atoms, their repulsion is rather weak; and when they part from five carbon atom, their repulsion is very weak.

Conjugation effect

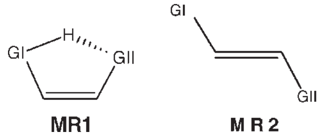
E_i in Scheme 5 reflects the comprehensive effects between nitro and amino groups in different molecules including induction effects, conjugation effects and intramolecular hydrogen bonds. In M12 of a trans-molecule, E_i mainly shows the sum of induction effect and intramolecular hydrogen bond between nitro and amino groups. The total effect 2 kJ/mol comprehensively reflects a slight repulsion between nitro and amino groups. This result agrees with the previous discussion about the interaction between nitro and amino groups.[17] In M13 with a nitro group and a *cis*-amino group, E_i indicates an integration of intramolecular hydrogen bond, conjugation effect and induction energy. Owing to the obvious intramolecular hydrogen bond and conjugation effect, there is the strongest attraction between nitro and amino groups, which leads to the most stable molecule. From the data in Scheme 5, we can find that there are more negative E_i when amino groups linked with the carbon atoms at even sites relative to the site of nitro group. This can be explained by resonant theory and is in agreement with a fact—introducing amino groups on even positions, particularly on 2-position relate to nitro group's site can apparently increase the molecular stability, due to the combination of the hydrogen bond, the induction effect and the conjugation effect.[17] Additionally, we can deduce that the resonant energy, that is the energy of



Scheme 4. E_i (unit in kJ/mol) between two nitro groups reflects the induction effect. The number denotes the site linked with the second nitro group (invisible) in dinitro pentane. For example, in M7, two nitro groups are linked with No 1 carbon atom



Scheme 5. E_i (unit in kJ/mol) between appointed nitro and amino groups reflects the comprehensive effect between them. The number denotes the site of the invisible amino group in the nitro-amino compound. The molecular configurations of M12–M20 have been illustrated in the scheme



Scheme 6. $E_{H\text{-bond}} = E(MR1)\text{-}E(MR2)$

Table 3. Calculated energies of intramolecular hydrogen bonds (unit in kJ/mol)

GI	GII	$E_{H\text{-bond}}$
NH_2	NO_2	18
NH_2	Cl	15
OH	Cl	21
NH_2	F	14
OH	NO_2	36
NH_2	OH	7
OH	OH	20

conjugation effect, between amino and nitro groups in bigger conjugated alkenes (the number of carbon atoms is above 4) is about 10 kJ/mol.

Intramolecular hydrogen bond

Seven groups of *cis-trans* isomers of derivatives of ethene are selected to approximately calculate intramolecular hydrogen bond energy. We can find from Scheme 6 that the hydrogen bond energy is in fact the energy difference between isomers MR1 and MR2. Here, the induction effect and conjugation effect between groups GI and GII in any group of isomers are taken equivalent, and some other interaction, for example, steric effect, strain forces, etc. are neglected. From Table 3, we found that the hydrogen bond energies are within 7–36 kJ/mol, and satisfied with the experimental criterion of hydrogen bond. We can also find that there is a strongest hydrogen bond between H atom on OH group and O atom on NO_2 group. This is due to the best condition of hydrogen bond formation of them among seven cases: the shorter O. . .H distance and the closer 180° of OH-ON angle. The offset of amino groups are restricted by C=C bond owing to their strong conjugation effect, which influences the hydrogen bond formation from amino groups and leads to the less hydrogen bond energies.

Application of the method to evaluate the interaction of appointed groups or atoms

Examples for some groups of molecules with the same skeletons

From above discussion, we can find that the sign of E_i of appointed groups can well reflect their interaction nature. For instance, the positive E_i among nitro groups (in M21–M29) implies the repulsion among them and the helplessness to molecular stability; whereas the negative E_i among nitro and amino groups (in M13–M20) implies the attraction among them and the helpfulness to molecular stability. Is there a quantitative relationship between E_i and the molecular stability? In this paper, we selected two groups of the simplest halogenated hydrocarbon to address the issue. Here, E_i are of all halogen atoms, and the molecular stabilities are measured by the total bond dissociation energies (ΣBDE) cited from Reference [18]. Up to the present, there have been many researches on the factors influencing BDE such as steric, inductive, resonant and field effects, and so forth.[19–29] Obviously, this study confirmed an E_i-ΣBDE correlation and offered a new approach to investigate BDE and molecular stabilities.

Very different from other halogenated methane, fluoromethane has increasing C—X and C—H BDEs with increasing F atom. It may be out of the common rule of organic chemistry, that is, the more the same atoms or groups displacing hydrogen atom on carbon atom, the less bond energy resulting from the more repulsion among these substitutes, for example, in Table 4, the more nitro group displaced, the less bond energy of C—Nitro. But we can surprisingly find that the BDE changes of all C—X and C—H bonds agree well with E_i of all X atoms. That is, the more negative E_i accords with the more BDE. It verifies again the introduced method. Obviously, we will draw a wrong conclusion

Table 4. E_i (kJ/mol) and BDE (kJ/mol) of $CH_{4-n}X_n$

X		CH_3X	CH_2X_2	CHX_3	CX_4
F	E_i	—	−45.4	−109.2	−154.7
	C–F	460.2 ± 8.4	496.2	533.9	546.8 ± 2.1
	C–H	423.8 ± 4.2	431.8	445.2	—
Cl	E_i	—	1.23	12.28	41.4
	C–Cl	350.2 ± 1.7	338.1	320.5 ± 6.3	296.6
	C–H	419.0 ± 2.3	407.1 ± 4.2	392.5 ± 2.5	—
Br	E_i	—	9.24	31.19	71.41
	C–Br	294.1 ± 2.1	290 ± 10	274.9 ± 13.0	228.9 ± 9.6
	C–H	427.2±2.4	417.1 ± 7.5	399.2 ± 8.4	—
I	E_i	—	15.87	44.44	91.26
	C–I	238.9 ± 2.1	217.1 ± 8.4	220.5 ± 33	192 ± 50
	C–H	433 ± 8.4	431.0 ± 8.4	423 ± 29	—
NO_2	E_i	—	43.5	115.5	202.3
	C–NO_2	260.7 ± 2.1	218.4	211.3	176.1

Table 5. E_i (kJ/mol) and BDE (kJ/mol) of halogenated methane

	E_i	BDE_{C-H}	BDE_{C-F}	BDE_{C-Cl}	BDE_{C-Br}
$CH F_2Cl$	−60.3	421.3 ± 8.4	462.3 ± 10	364 ± 8	—
$CH FCl_2$	−19.2	410.9 ± 8.4	453 ± 23	346.0 ± 13.4	—
$CHCl_2Br$	12.8	387 ± 21	—	310 ± 17	250 ± 21
$CHClBr_2$	21.6	371 ± 21	—	299 ± 21	244 ± 21
CF_3Cl	−100.7		511.7	365.3	
CF_2Cl_2	−48.7		482.0 ± 10.5	333.9 ± 10.5	
$CFCl_3$	−0.8		439.3 ± 4	320.9 ± 8.4	
CCl_3Br	41.1			287 ± 10.5	231.4 ± 4.2
CCl_2Br_2	50.4			274 ± 17	225.5 ± 17
$CClBr_3$	60.4			261.5 ± 10.5	210.9 ± 10.5
CH_4		439.3 ± 0.4			

that the more substituted F atoms can result in the less C—F BDE if we only consider the repulsion among F atoms.

The negative E_i of F atoms in fluoromethane in Table 4 shows there are strong attractions between F atoms through carbon atom, although they have the same negative charges which can result in the coulomb repulsions. In fact, all C—F bonds and C—H bonds are shortened when F atoms increasing in molecules. It tells us the overlap of atomic orbits increasing on not only C—F, but also other bonds. Therefore, E_i of X atoms in halogenated methane can reflect the nature and strength of the interaction of X atoms. That is to say, through a carbon atom, all F atoms are attractive one another, unlike other halogen atoms or nitro groups. It is the unique characteristic of fluoride.

By means of E_i of halogen atoms or BDEs in relevant molecules, Table 5 confirms a fact that there is an attraction between F atoms and other halogen atoms, and the more F atoms the more attraction; whereas the repulsion among Cl and Br atoms, and the more Br atoms the more repulsion. Apparently, E_i of all halogen atoms has a comprehensive sense of molecular stability, whereas BDE only reflects the stability of an individual bond. That is, E_i and BDE have comprehensive and individual senses, respectively. Then, the total BDE, ΣBDE, has a comprehensive sense too and may be dependent on E_i. Therefore, the E_i of all halogen atoms *versus* ΣBDE of halogenated methane was plotted on Fig. 1. We can find there is a good linear E_i-ΣBDE dependence, and accordingly, E_i is also a useful tool to evaluate the molecular stability. Figure 1 also demonstrates a decreasing order of ΣBDE with an increasing order of E_i when increasing substituted halogen atoms from F to Cl, Br, and I atoms. For example, ΣBDE deceases and E_i increases as an order of CF_4, CCl_4, CBr_4, and CI_4, or an order of CF_4, CF_3Cl, CF_2Cl_2, $CFCl_3$, and CCl_4.

We also calculated halogenated ethane (for isomers, only the most stable one with the least E_i was discussed). This case is similar to halogenated methane. That is to say, there is also an approximate linear E_i-ΣBDE correlation for halogenated ethane (Fig. 2). We also find ΣBDE deceases and E_i increases as an order of C_2F_6, C_2Cl_6, C_2Br_6, and C_2I_6, or an order of C_2F_6, C_2F_5Cl, $C_2F_4Cl_2$, $C_2F_3Cl_3$, $C_2F_2Cl_4$, C_2FCl_5, and C_2Cl_6. On the one hand, it verifies again that F atoms can decrease the E_i of all substituted halogen atoms and increase the molecular stability. On the other hand, it verifies again that E_i can be used as a tool to assess the molecular stability only for a separate group of analogues.

Example for the appointed groups in different molecules

The previous work[10] and above section confirmed that E_i of all substitution groups or nonhydrogen atoms around a molecular skeleton is a tool to evaluate molecular stability and has a comprehensive sense. Here, as a complement, we will discuss the application of E_i to the appointed groups in different on an individual sense. That is to say, the interaction of appointed groups in different molecules is concerned. It should be emphasized that the designed isodesmic reactions for E_i

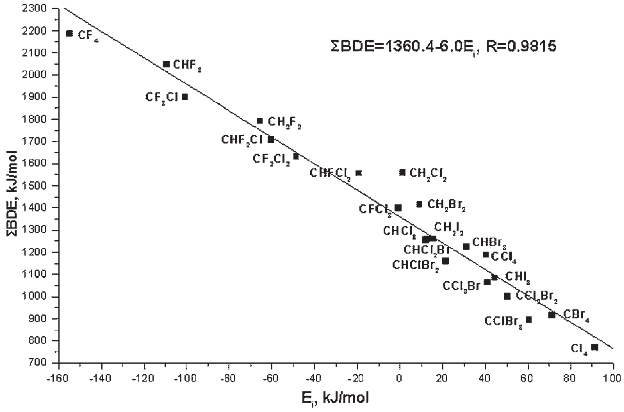


Figure 1. E_i of all halogen atoms *versus* ΣBDE of halogenated methane

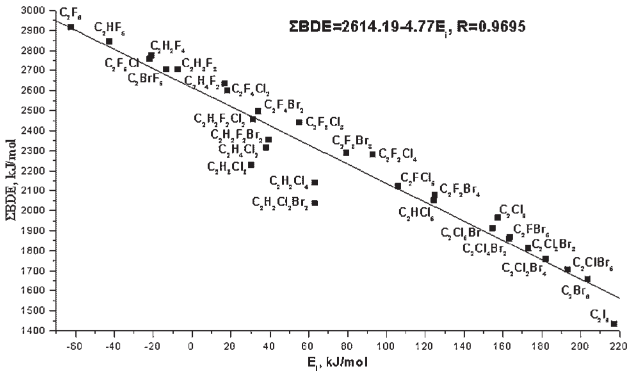
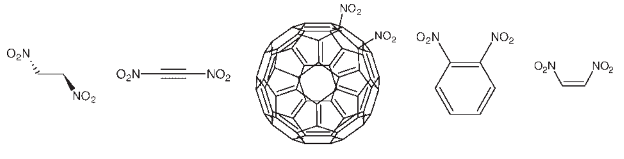
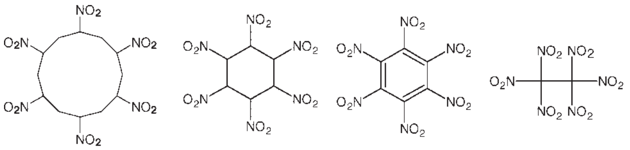


Figure 2. E_i of all halogen atoms *versus* ΣBDE in halogenated ethane



M21 21 **M22 29** **M23 41** **M24 58** **M25 89**

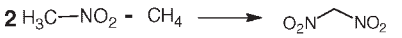
Scheme 7. E_i (unit in kJ/mol) of two nitro groups in different chemical environments



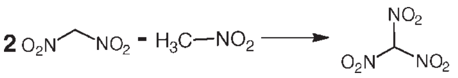
M26 166 **M27 181** **M28 3541** **M29 3891**

Scheme 8. E_i (unit in kJ/mol) of six nitro groups in different chemical environments

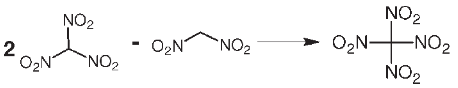
calculation for the appointed groups in different molecules are different. For example, following reactions indicated these differences. Equations Eqn. 3–53-5 are designed for calculating E_i of two nitro groups in dinitro-, trinitro- and tetranitromethane, respectively. In fact, designing isodesmic reactions for E_i calculation in Section 'Validity confirmation of the new method' are also different from one another.



(3)



(4)



(5)

In above nitromethane, the length of C—NO_2 bond increases from 1.543 Å in dinitromethane to 1.548 Å in trinitromethane and 1.582 Å in tetranitromethane, and Mulliken charges on nitro groups decrease from −0.190e to −0.152e and −0.050e can accordingly lessen the repulsion between two nitro groups. By means of the new method, we obtained the calculated E_i of two nitro groups in dinitro-, trinitro- and tetranitromethane which is 44, 29 and 15 kJ/mol, respectively, showing the repulsion decrease. It verifies my new approach.

From Eqns 1 and 2, we can find the most advantage of the method introduced in this paper is that E_i of any two or more appointed groups within a molecule can quantitatively reflect the nature (attraction or repulsion) and strength of their interaction. Schemes 7 and 8 give illustrations of different E_i of two and six nitro groups in different molecules, respectively. Section 'Steric effect' belongs to this case too (the isodesmic reactions can be seen in Supporting Information). In Scheme 7, two *ortho*-positional nitro groups in different molecules have different E_i. Owing to the free rotation the C—NO_2, M21 can have the least E_i of two nitro groups (repulsion mainly). In M22, two nitro groups linked with abundant electron body C═C bond have the best orientation to avoid their repulsion, and therefore less E_i than M23, M24 and M25. Apparently, the more the linked structure's ability to donate electrons to nitro groups can more decrease the repulsion between two linked nitro groups. C60 has more ability to offer electrons than benzene ring and C═C, so, M23 has less E_i than M24 or M25 accordingly.

Scheme 8 shows the case of six nitro groups in different chemical environments (molecules). Owing to the free rotation of C—NO_2 bonds and the large distances among nitro groups, M26 has the least E_i denoting the least repulsion. But M27 has the larger E_i for the closer distances among nitro groups, even though C—NO_2 bonds can also rotate freely. Obviously, M28 has more E_i due to rotation restriction of C—NO_2 bonds and closer distances among nitro groups, and M29 has the largest E_i due to the electron deficiency of C—C and the closest distances among nitro groups. Theoretical qualitative descriptions are in good agreement with quantitative calculated results. At the same time, we can also find the abundant electron body linked with nitro groups can efficiently decrease the repulsion among nitro groups.

CONCLUSION

A new approach reported in this paper is necessary in case of the inefficiency of interaction descriptions of appointed groups or nonhydrogen atoms within a molecule. The method can just quantitatively evaluate these interactions by designing unique isodesmic reactions, further calculating their energy changes, and getting so-called interaction energy (E_i). Typically, there are two applications of the method: (1) for any group of molecules with the same skeleton, E_i of all substitution groups or nonhydrogen atoms can be used to compare their molecular stabilities; (2) for the appointed groups in different molecules, E_i of them can reveal the nature (attraction or repulsion) and the strength of their interaction. All these indicated that E_i is a useful tool to describe the interaction of appointed groups or nonhydrogen atoms.

SUPPORTING INFORMATION

The total energies of some molecules mentioned in the paper and some illustrations for designing isodesmic reactions to calculate mutual effect energies were contained in supporting information.

Acknowledgements

The financial support from China National Project 973 and CAEP's funds (No 626010918) was greatly appreciated.

REFERENCES

[1] S.-C. Xu, *Organic Chemistry (Version 2)*, High Education Press, Beijing, 1993.
[2] O. Exner, S. Bohm, *J. Org. Chem.* **2002**, *67*, 6320.
[3] L. Liu, Y.-H. Cheng, Y. Fu, R. Chen, Q.-X. Guo, *J. Chem. Inf. Comput. Sci.* **2002**, *42*, 1164.
[4] K. B. Wiberg, *J. Org. Chem.* **2003**, *68*, 875.
[5] Y.-H. Cheng, X. Zhao, K.-S. Song, L. Liu, Q.-X. Guo, *J. Org. Chem.* **2002**, *67*, 6638.
[6] K. B. Clark, D. D. M. Wayner, *J. Am. Chem. Soc.* **1991**, *113*, 9363.
[7] W. M. Nau, *J. Phys. Org. Chem.* **1997**, *10*, 445.

[8] J.-P. Cheng, B. Liu, Y. Zhao, Z. Wen, Y. Sun, *J. Am. Chem. Soc.* **2000**, *122*.

[9] L. Liu, Y. Fu, R. Liu, R.-Q. Li, Q.-X. Guo, *J. Chem. Inf. Comput. Sci.* **2004**, *44*, 652.

[10] C. Zhang, *J. Phys. Chem. A* **2006**, *110*, 14029.

[11] H. Dong, F. Zhou, *High Energetic Explosives and their Relatives*, Scientific Press, Beijing, 1994.

[12] B. Delley, *J. Chem. Phys.* **1990**, *92*, 508.

[13] B. Delley, *J. Chem. Phys.* **2000**, *113*, 7756.

[14] *Material Studio 3.0*, Accelrys, Inc., San Diego, CA, 2003.

[15] C. Zhang, Y. Shu, X. Wang, X. Zhao, B. Tan, R. Peng, *J. Phys. Chem. A.* **2005**, *109*, 6592.

[16] C. Zhang, Y. Shu, Y. Huang, X. Zhao, H. Dong, *J. Phys. Chem. B.* **2005**, *109*, 8978.

[17] C. Zhang, *Chem. Phys.* **2006**, *324*, 547.

[18] Y. Luo, *A Handbook of Chemical Bond Energy*, Scientific Press, Beijing, 2005.

[19] Y. Fu, L. Liu, R. Liu, Q.-X. Guo, *J. Phys. Org. Chem.* **2005**, *18*, (6) 529.

[20] K.-S. Song, L. Liu, Q.-X. Guo, *Tetrahedron.* **2004**, *60*(44), 9909.

[21] K. U. Ingold, J. S. Wright, *J. Chem. Educ.* **2000**, *77*, 1062.

[22] C. Z. Cao, Y. B. Lin. *Chin. J. Org. Chem.* **2003**, *23*, 207.

[23] D. F. McMillen, D. M. Golden, *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

[24] S. J. Blanksby, G. B. Ellison, *Acc. Chem. Res.* **2003**, *36*, 255.

[25] A. R. Cherkasov, M. Jonsson, V. I. Galkin, R. A. Cherkasov, *Russ. Chem. Rev.* **2001**, *70*, 1.

[26] J. Berkowitz, G. B. Ellison, D. Gutman, *J. Phys. Chem.* **1994**, *98*, 2744.

[27] F. H. Bordwell, X.-M. Zhang, *Acc. Chem. Res.* **1993**, *26*, 510.

[28] L. J. J. Laarhoven, P. Mulder, D. D. M. Wayner, *Acc. Chem. Res.* **1999**, *32*, 342.

[29] D. J. Henry, C. J. Parkinson, P. M. Mayer, L. Radom, *J. Phys. Chem. A* **2001**, *105*, 6750.