

Relationships for the Impact Sensitivities of Energetic C-Nitro Compounds Based on Bond Dissociation Energy

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The ZPE-corrected C–NO₂ bond dissociation energies (BDE_{ZPE}) of a series of model C-nitro compounds and 26 energetic C-nitro compounds have been calculated using density functional theory methods. Computed results show that for C-nitro compounds the UB3LYP calculated BDE_{ZPE} is less than the UB3P86 using the 6-31G** basis set, and the UB3P86 BDE_{ZPE} changes slightly with the basis set varying from 6-31G** to 6-31++G**. For the series of model C-nitro compounds with different chemical skeletons, it is drawn from NBO analysis that the order of BDE_{ZPE} is not only in line with that of the NAO bond order but also with that of the energy gap between C–NO₂ bonding and antibonding orbitals. It is found that for the energetic C-nitro compounds whose drop energies (E_{dr}) are below 24.5 J a good linear correlation exists between E_{dr} and BDE_{ZPE}, implying that these compounds ignite through the C–NO₂ dissociation mechanism. After excluding the so-called trinitrotoluene mechanism compounds, a polynomial correlation of $\ln(E_{\text{dr}})$ with the BDE_{ZPE} calculated at density functional theory levels has been established successfully for the 18 C–NO₂ dissociation energetic C-nitro compounds.

1. Introduction

A deep understanding of the factors affecting the sensitivities of energetic compounds plays an important role in designing less sensitive high-performance energetic systems to meet the requirements of future military and civil applications. With respect to other sensitivities, impact sensitivity is the most commonly used measure of an explosive to ignite and is used to judge the stability of energetic compound to external stimuli. Experimentally, the impact sensitivity increases as the 50% impact height (H_{50}) decreases, which is the height at which there is a 50% probability of ignition when impact tests apply a force to a sample of energetic material by a standard hammer falling from various heights.

Energetic C-nitro compounds are of vital importance. Over the past several decades, the structure–sensitivity relationships of these compounds have been frequently investigated theoretically and experimentally. In the past, Kamlet proposed rough linear relationships between $\log(H_{50})$ and oxygen balance (OB₁₀₀) for specific classes of compounds, e.g., trinitromethyl and *gem*-dinitro compounds.¹ Later on, the impact reactivities of energetic compounds have been studied with quantum chemistry and molecular dynamics methods. The C–NO₂ bond strength (e.g., bond order, bond dissociation energy, and midpoint potential) were found to be related to the impact sensitivity for a series of energetic compounds,^{2–9} supporting that the strength of C–NO₂ bond in energetic C-nitro molecules might be of key importance in determining sensitivities to impact and shock. For example, about a decade ago Wu et al.⁷ reported a DFT study of 14 energetic compounds including TATB, DATB, TNT, and TNB and a linear relationship between ratio of bond dissociation energy to decomposition energy and $\log(H_{50})$, although it is unrea-

sonable to consider that TNT decomposes through the C–NO₂ dissociation mechanism under impact and shock.^{10,11} In 2006, a nearly linear correlation between H_{50} and ratio of bond dissociation energy to total molecular energy for nitroaromatic explosives with nitroalkyl was provided by Song and co-workers.⁸ On the other hand, the impact sensitivity was also found to be related to the NMR chemical shift in reaction center, the heat of fusion, the low-temperature thermolysis parameter, and the intermolecular interaction by Zeman.¹²

However, the above qualitative or quantitative relationships were restricted within a special class of energetic compounds. Is it possible to construct a relatively comprehensive quantitative relationship for energetic C-nitro compounds? For this purpose, this work also uses the C–NO₂ bond dissociation energy to characterize the C–NO₂ bond strength, which is more convenient to compare with other types of energetic compounds than electronic structure parameters. In the effort to get a reliable correlation for the impact sensitivities of energetic C-nitro compounds, the influence of C–NO₂ bond dissociation energy on impact sensitivity has been discussed in detail, and the quantitative relationships of impact sensitivity with C–NO₂ bond dissociation energy have been suggested, which are important for designing functional energetic compound and evaluating the stability of energetic compound. Additionally, the characteristics for low-sensitive C–NO₂ energetic compounds is analyzed.

2. Computational Methods and Details

As mentioned above, for energetic C-nitro compounds the C–NO₂ bond dissociation energy is not only effective for characterizing the C–NO₂ bond stability, but also possibly a major factor affecting the sensitivity. By employing the C–NO₂ bond

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TABLE 1: UB3LYP and UB3P86 Calculated Zero-Point Energy Corrections (in kJ/mol) and ZPE-Corrected C–NO₂ Bond Dissociation Energies (in kJ/mol) of Model C-Nitro Compounds with Different Frameworks Using the 6-31G Basis Set**

compound	UB3LYP		UB3P86	
	ZPEC	BDE _{ZPE}	ZPEC	BDE _{ZPE}
nitromethane	−19.8	238.3	−29.9	244.1
nitrocyclopropane	−13.9	281.1	−24.1	288.1
nitrocyclobutane	−19.6	237.9	−26.5	249.9
nitrocyclohexane	−13.4	239.1	−23.9	245.8
nitroethene	−15.1	284.6	−25.2	290.5
nitroethyne	−14.1	315.3	−21.1	322.8
nitrobenzene	−8.5	298.9	−18.5	305.1
nitropyrazine	−6.5	255.9	−16.8	263.2
nitro-1,3,5-triazine	−6.6	240.1	−16.8	246.9
nitro-1,2,4,5-tetraazine	−7.7	240.5	−17.9	247.8

cleavage reaction $\text{RCNO}_2 \rightarrow \text{RC}^\bullet + \text{NO}_2^\bullet$, the C–NO₂ bond dissociation energy (BDE) is calculated as

$$\text{BDE} = E(\text{RC}^\bullet) + E(\text{NO}_2^\bullet) - E(\text{RCNO}_2) \quad (1)$$

where E is the total energy. The C–NO₂ bond dissociation energy (BDE_{ZPE}) corrected for zero-point energy (ZPE) is

$$\text{BDE}_{\text{ZPE}} = \text{BDE} + \text{ZPEC} \quad (2)$$

where ZPEC is the zero-point energy correction. In order to analyze the influence of chemical framework on the BDE and to correlate the impact sensitivity with the BDE, a series of model C-nitro compounds and 26 energetic C-nitro compounds have been selected here. Because the density functional theory methods consider the electronic correlation effects and are less demanding from the point view of computation, especially the Becke three-parameter hybrid functionals (e.g., B3LYP^{13,14} and B3P86¹⁵) are widely applied to investigate energetic compounds.^{7–9,16} In this work, all geometries including molecule and free radical are fully optimized using the UB3LYP method and the 6-31G** basis set. In addition, the density functional UB3P86 method is also taken into account to discuss roughly the influence of density functional theory methods on calculated results. Vibrational analysis is performed at the same level for each stationary point to verify a minimum energy structure and to provide the zero-point energy. All quantum chemistry calculations have been carried out with the Gaussian 03 program package.¹⁷

3. Results and Discussion

3.1. C–NO₂ Bond Dissociation Energies of a Series of Model C-Nitro Compound. Molecular framework is a major factor influencing the C–NO₂ bond strength that is described using the bond dissociation energy in this work. The calculated

TABLE 3: UB3LYP and UB3P86 Calculated Zero-Point Energy Corrections (in kJ/mol) and ZPE-Corrected C–NO₂ Bond Dissociation Energies (in kJ/mol) of Model C-Nitro Compounds Using the 6-31++G Basis Set**

compound	UB3LYP		UB3P86	
	ZPEC	BDE _{ZPE}	ZPEC	BDE _{ZPE}
nitromethane	−29.4	226.6	−29.6	243.5
nitrocyclopropane	−23.9	266.8	−23.9	285.5
nitrocyclobutane	−26.5	230.6	−27.5	248.5
nitrocyclohexane	−24.0	225.6	−23.8	244.0
nitroethene	−25.2	269.1	−25.1	286.8
nitroethyne	−24.1	299.3	−20.9	318.3
nitrobenzene	−18.4	281.3	−18.1	300.0
nitropyrazine	−16.3	238.4	−16.5	258.2
nitro-1,3,5-triazine	−16.5	225.9	−16.6	244.4
nitro-1,2,4,5-tetraazine	−17.7	226.5	−17.7	245.7

C–NO₂ bond dissociation energies (BDE_{ZPE}) of a series of the model C-nitro compounds with different chemical skeletons employing the unrestricted B3LYP and B3P86 methods and the 6-31G** basis set are listed in Table 1. Table 1 shows that the UB3LYP calculated BDE_{ZPE} is 5–12 kJ/mol less than the UB3P86 systematically with the 6-31G** basis set. For nitromethane, the calculated BDE_{ZPE} from UB3LYP and UB3P86 methods are close to the experimental value (238.9 kJ/mol).¹⁸

Insofar as nitrocycloalkanes are concerned, due to the ring strain in cyclopropane, which weakens the C–C bond in the ring and thereby strengthens the C–NO₂ bond, the BDE_{ZPE} of nitrocyclopropane is much larger than those of nitrocyclobutane and nitrocyclohexane, which approach that of nitromethane. The BDE_{ZPE} of nitroethyne can reach 315.3 kJ/mol at the UB3LYP/6-31G** level, being 30.7 kJ/mol larger than that of nitroethene, implying that nitroethyne is very stable and insensitive. For the model C-nitro compounds studied here, the order of BDE_{ZPE} is as follows: nitroethyne > nitrobenzene > nitroethene ≈ nitrocyclopropane > nitropyrazine > nitro-1,3,5-triazine ≈ nitro-1,2,4,5-tetraazine ≈ nitrocyclohexane. In order to further analyze the reason that molecular framework affects the C–NO₂ bond dissociation energy, the occupancy (δ) and energy (ϵ) for C–NO₂ bonding and antibonding orbitals ($\sigma_{\text{C-NO}_2}$ and $\sigma^*_{\text{C-NO}_2}$) and the NAO bond order ($\beta_{\text{C-NO}_2}$) for C–NO₂ bond obtained by natural bond orbital (NBO) analysis^{19–21} at the UB3LYP/6-31G** level are listed in Table 2. For the series of model C-nitro compounds, the δ values for $\sigma_{\text{C-NO}_2}$ and $\sigma^*_{\text{C-NO}_2}$ have a very small change, but the energy gap ($\Delta\epsilon_{\text{C-NO}_2}$) between $\sigma_{\text{C-NO}_2}$ and $\sigma^*_{\text{C-NO}_2}$ differs largely. Especially for these model C-nitro compounds the order of BDE_{ZPE} is consistent not only with that of $\Delta\epsilon_{\text{C-NO}_2}$ but also with that of $\beta_{\text{C-NO}_2}$, verifying that the BDE_{ZPE} can reflect the influence of chemical framework on the C–NO₂ bond strength.

Table 3 lists the calculated BDE_{ZPE} using the 6-31++G** basis set. Compared with the 6-31++G**, for UB3LYP

TABLE 2: Natural Bond Orbital Analysis Results for a Series of Model C-Nitro Compounds at the UB3LYP/6-31G Level^a**

compound	$\sigma_{\text{C-NO}_2}$		$\sigma^*_{\text{C-NO}_2}$		$\Delta\epsilon_{\text{C-NO}_2}$ (hartrees)	$\beta_{\text{C-NO}_2}$	$r_{\text{C-NO}_2}$ (Å)
	δ (e)	ϵ (hartrees)	δ (e)	ϵ (hartrees)			
nitromethane	1.995	−0.7904	0.084	0.2188	1.0092	0.750	1.499
nitrocyclopropane	1.992	−0.8101	0.012	0.2639	1.0740	0.790	1.472
nitrocyclobutane	1.992	−0.7845	0.108	0.2391	1.0236	0.753	1.504
nitrocyclohexane	1.988	−0.7678	0.104	0.2329	1.0007	0.742	1.516
nitroethene	1.991	−0.8198	0.099	0.2695	1.0893	0.805	1.466
nitroethyne	1.991	−0.9074	0.094	0.3013	1.2087	0.898	1.402
nitrobenzene	1.990	−0.8133	0.105	0.2764	1.0898	0.809	1.474
nitropyrazine	1.988	−0.8176	0.143	0.2314	1.0490	0.771	1.493
nitro-1,3,5-triazine	1.986	−0.8210	0.162	0.2030	1.0240	0.749	1.502
nitro-1,2,4,5-tetraazine	1.984	−0.8470	0.148	0.1987	1.0456	0.761	1.489

^a $\Delta\epsilon_{\text{C-NO}_2}$ is equal to $\epsilon(\sigma^*_{\text{C-NO}_2}) - \epsilon(\sigma_{\text{C-NO}_2})$, and $r_{\text{C-NO}_2}$ is the C–NO₂ bond length.

TABLE 4: Impact Sensitivities of Energetic C-Nitro Compounds (E_{dr} Is the Drop Energy)

no.	acronym	chemical name	H_{50} (cm)	E_{dr} (J)
1	TNB	1,3,5-trinitrobenzene	100/2.5 kg ^a	24.5
2	MATB	1-amino-2,4,6-trinitrobenzene	177/2.5 kg ^a	43.4
3	DATB	1,3-diamino-2,4,6-trinitrobenzene	>200/2.5 kg ^d	78.5 ^e
4	TATB	1,3,5-triamino-2,4,6-trinitrobenzene	>200/2.5 kg ^d	120.2 ^e
5	LLM-105	2,6-diamino-3,5-dinitropyrazine 1-oxide	117/2.5 kg ^b	28.7
6	FOX-7	1,1-diamino-2,2-dinitroethene	72/5 kg ^b	35.2
7	TNT	2,4,6-trinitrotoluene	160/2.5 kg ^a	39.2
8	NTO	3-nitro-1,2,4-triazole-5-one	291/2.5 kg ^a	71.3
9	DAPA	3,5-diamino-2,4,6-trinitrophenol	112/2.5 kg ^c	27.4
10	ADNBF	7-amino-4,6-dinitrobenzofuroxan	100/2.5 kg ^d	24.5
11	APA	3-amino-2,4,6-trinitrophenol	138/2.5 kg ^c	33.8
12	ATNT	3-amino-2,4,6-trinitrotoluene	174/2.5 kg ^d	42.6
13	DATNT	3,5-diamino-2,4,6-trinitrotoluene	239/2.5 kg ^d	58.6
14	CL-14	5,7-amino-4,6-dinitrobenzofuroxan	120/2.5 kg ^d	29.4
15	DIPAM	3,3'-diamino-2,2',4,4',6,6'-hexanitrobiphenyl	67/2.5 kg ^d	16.4
16	DMOTNB	1,3-dimethoxy-2,4,6-trinitrobenzene	251/2.5 kg ^c	61.5
17	DNBF	4,6-dinitrobenzofuroxan	76/2.5 kg ^c	18.6
18	DNPP	3,6-dinitropyrazolo[4,3-c]pyrazole	68/5 kg ^b	33.3
19	LLM-119	1,4-diamino-3,6-dinitropyrazolo[4,3-c]pyrazole	24/5 kg ^b	11.8
20	HNAB	2,2',4,4',6,6'-hexanitroazobenzene	32/2.5 kg ^a	7.8
21	HNBP	2,2',4,4',6,6'-hexanitrobiphenyl	70/2.5 kg ^c	17.2
22	MDNT	4-methyl-3,5-dinitro-1,2,4-triazole	155/2.5 kg ^a	38.0
23	PNA	pentanitroaniline	22/2.5 kg ^c	5.4
24	PNB	pentanitrobenzene	11/2.5 kg ^c	2.7
25	TetNB	1,2,3,5-tetranitrobenzene	28/2.5 kg ^c	6.9
26	TNI	2,4,5-trinitroimidazole	68/2.5 kg ^a	16.7

^a Reference 22a. ^b Reference 23. ^c Reference 22b. ^d Reference 24. ^e They can be derived from data in ref 25.

TABLE 5: UB3LYP and UB3P86 Calculated Total Energies, Zero-Point Energy Corrections, and ZPE-Corrected C–NO₂ Bond Dissociation Energies of Energetic C-Nitro Compounds Using 6-31G** Basis Set

compound	UB3LYP			UB3P86		
	E_{tot} (hartrees)	ZPEC (kJ/mol)	BDE _{ZPE} (kJ/mol)	E_{tot} (hartrees)	ZPEC (kJ/mol)	BDE _{ZPE} (kJ/mol)
TNB	−845.741483	−6.7	278.1	−847.664387	−16.8	284.2
MATB	−901.116435	−7.4	295.0	−903.187365	−17.5	301.5
DATB	−956.489821	−9.3	302.9	−958.709160	−19.0	313.8
TATB	−1011.856489	−3.2	354.8	−1014.224665	−13.6	370.3
LLM-105	−859.224276	−8.2	273.8	−861.192566	−18.6	282.7
FOX-7	−598.325244	−7.2	290.4	−599.685011	−17.1	301.8
TNT	−885.053127	−7.0	256.8	−887.123331	−17.2	263.5
NTO	−521.982205	−8.7	280.6	−523.161306	−18.5	289.6
DAPA	−1031.709193	−6.7	279.9	−1034.072731	−16.7	289.3
ADNBF	−955.205658	−7.1	289.3	−957.384340	−17.3	296.1
APA	−976.339221	−6.9	274.3	−978.554157	−16.9	282.9
ATNT	−940.424284	−7.5	271.3	−942.642556	−17.6	278.3
DATNT	−995.791951	−8.8	266.7	−998.158693	−18.8	275.9
CL-14	−1010.577466	−7.8	318.0	−1012.904532	−18.2	327.5
DIPAM	−1801.001214	−6.4	275.2	−1805.110515	−16.4	283.8
DMOTNB	−1074.759761	−5.2	224.1	−1077.256336	−15.4	226.1
DNBF	−899.823055	−7.1	282.5	−901.854044	−17.2	288.9
DNPP	−782.765199	−7.8	300.5	−784.554365	−17.8	307.2
LLM-119	−893.406818	−8.6	308.1	−895.487284	−18.7	315.9
HNAB	−1799.685110	−6.3	238.4	−1803.743818	−16.3	243.8
HNBP	−1690.255859	−6.4	279.1	−1694.068648	−16.4	285.7
MDNT	−690.521726	−6.7	265.5	−692.092296	−16.6	273.5
PNA	−1310.031983	−6.2	239.7	−1312.88159	−16.4	247.6
PNB	−1254.659635	−5.7	217.4	−1257.361097	−16.0	224.2
TetNB	−1050.200938	−5.4	220.7	−1052.513224	−15.7	228.0
TNI	−839.677502	−4.6	252.5	−841.493558	−14.8	258.9

^a E_{tot} is the total energy not corrected for ZPE.

method the 6-31G** calculated BDE_{ZPE} increases by 7–18 kJ/mol, but for UB3P86 method it changes slightly. Therefore, for UB3LYP and UB3P86 methods it is appropriate to adopt the basis set 6-31G** to calculate the C–NO₂ bond dissociation energy.

3.2. Influence of C–NO₂ Bond Dissociation Energy on Impact Sensitivity. Table 4 displays the experimental impact sensitivities of 26 energetic C-nitro compounds. The drop energy (E_{dr}) is transformed by mgH_{50} , where m is the mass of drop hammer and g is the acceleration due to gravity. Recently, the

low-sensitive energetic compounds have been focused on worldwide. A look at Table 4 indicates that it is rational to designate the energetic compound as low-sensitive if its drop energy ≥ 24.5 J, which is just the impact sensitivities of low-sensitive energetic compounds TNB and ADNBF. The E_{dr} values of the 17 energetic C-nitro compounds in Table 4 can reach 24.5 J. In order to discuss the influence of C–NO₂ bond strength on the impact sensitivity, Table 5 gives UB3LYP and UB3P86 calculated BDE_{ZPE} of the 26 energetic C-nitro compounds using the 6-31G** basis set. It is worth mentioning

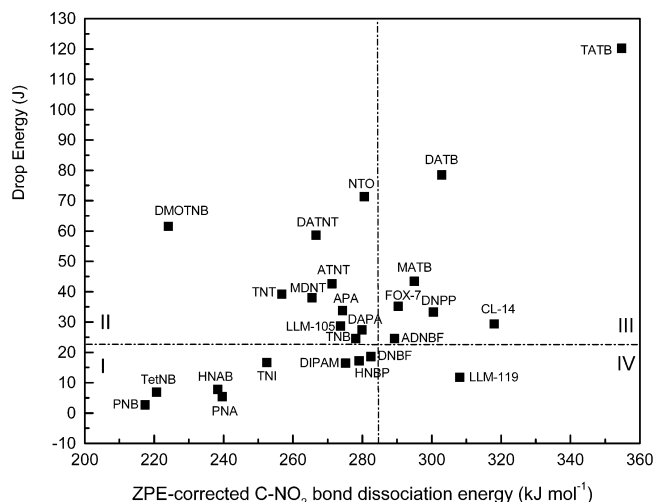


Figure 1. Plot of drop energy against UB3LYP/6-31G** calculated ZPE-corrected C–NO₂ bond dissociation energy for 26 energetic C-nitro compounds.

that if there are several C–NO₂ bonds in a molecule, the C–NO₂ bond dissociation energy listed here is the least. For example, there are two different C–NO₂ bonds in DATB; the listed C–NO₂ bond dissociation energy is the smaller one.

Figure 1 depicts the plot of BDE_{ZPE} versus E_{dr} for the 26 energetic C-nitro compounds. According to the values of E_{dr} and BDE_{ZPE} , the 26 compounds can be divided into four classes (see Figure 1): I, II, III, and IV. The compounds in classes II and III have low sensitivity. At the UB3LYP/6-31G** level the BDE_{ZPE} for classes I and II are in the range of 200–285 kJ/mol, and for classes III and IV they are over 285 kJ/mol. A glance at Figure 1 demonstrates that for class I the E_{dr} shows a good correlation with the BDE_{ZPE} , implying that the compounds in class I initiate by means of C–NO₂ dissociation. For class III the E_{dr} increases generally as the BDE_{ZPE} becomes larger. It is obvious that if the $BDE_{ZPE} \geq 285$ kJ/mol at the UB3LYP/6-31G** level the energetic C-nitro compounds have most probably low sensitivity with the exception of the compound LLM-119 contained in class IV, whose experimental impact sensitivity is suspect because the introduction of $-NH_2$ into DNPP improves the C–NO₂ bond stability and forms intra- and intermolecular hydrogen bonds in LLM-119. For class II it is difficult to find the correlation of E_{dr} with BDE_{ZPE} , which is because the energetic compounds in class II take different initiation pathways. From the experimental results obtained by Bulusu¹¹ and Zeman^{10,26} et al., it can be confirmed or deduced that compounds TNT, ATNT, DATNT, MDNT, DMOTNB, APA, and DAPA dissociate through the so-called trinitrotoluene mechanism under impact, and so for these compounds it is irrational to connect the impact sensitivity with the C–NO₂ bond strength.

3.3. Quantitative Relationships for the Impact Sensitivities of Energetic C-Nitro Compounds. It is reasonable to create the correlation of the impact sensitivity with the C–NO₂ bond dissociation energy for the energetic compounds that decompose through the C–NO₂ fission mechanism. First, when E_{dr} and BDE_{ZPE} are in J and kJ/mol, respectively, for the analogues TNB, MATB, DATB, and TATB the fit relationship between E_{dr} and BDE_{ZPE} at the UB3LYP/6-31G** level is $E_{dr} = -309.49 + 1.22243 \times BDE_{ZPE}$ where the correlation coefficient (r) is 0.959, and for the analogues DNBF, ADNBF, and CL-14 the relationship is $E_{dr} = -54.38 + 0.26484 \times BDE_{ZPE}$, where $r = 0.923$, displaying that for these analogues the impact sensitivity is closely related to the BDE_{ZPE} . Second, for class I the fit linear relationship at the UB3LYP/6-31G** level is $E_{dr} = -45.08 + 0.22557 \times BDE_{ZPE}$ ($r = 0.918$), implying that the impact sensitivities of energetic C-nitro compounds whose drop energies are below the 24.5 J line have a good correlation with the BDE_{ZPE} except for the suspect LLM-119.

For the energetic C-nitro compounds studied here, the residual 18 compounds fall into C–NO₂ dissociation mechanism after excluding the trinitrotoluene mechanism compounds and the suspect LLM-119. After several trials the following polynomial correlation between $\ln(E_{dr})$ and BDE_{ZPE} for the 18 C–NO₂ fission energetic C-nitro compounds is suggested

$$\ln(E_{dr}) = a_1 + a_2 BDE_{ZPE} + a_3 BDE_{ZPE}^2 + a_4 BDE_{ZPE}^3 + \dots + a_n x_n \quad (3)$$

where a_i ($i = 1, 2, 3, \dots, n$) is the adjustable parameter, which can be determined using the multiple linear regression technique. When E_{dr} and BDE_{ZPE} are in J and kJ/mol, respectively, using the UB3LYP/6-31G** calculated BDE_{ZPE} the regressed results of eq 3 for the 18 compounds are listed in Table 6, where R is the total correlation coefficient. The values of R show that the accuracy of the correlation of $\ln(E_{dr})$ with BDE_{ZPE} can be aptly improved as n increases, but it is appropriate while n reaches 4. At $n = 4$ the R value reflects that the regression is relatively successful. As can be seen from Figure 2, there exist two points that the fit drop energy differs from the experimental value largely, owing to the experimental uncertainty in the drop hammer test of impact sensitivity²⁷ and to the influence of other factors on impact sensitivity. For instance, recently Politzer et al. have found that the impact sensitivity is related to the intermolecular interaction in the crystal lattice.²⁸ Additionally, Table 6 shows that the UB3P86/6-31G** calculated BDE_{ZPE} of the energetic C-nitro compounds also obey the above correlation.

4. Conclusions

This work has calculated the ZPE-corrected C–NO₂ bond dissociation energies of a series of model C-nitro compounds

TABLE 6: Regressed Results for the Proposed Correlation Eq 3 of the Impact Sensitivities of 18 C–NO₂ Fission Energetic C-Nitro Compounds with the C–NO₂ Bond Dissociation Energies at Different Density Functional Theory Levels When E_{dr} and BDE_{ZPE} Are in J and kJ/mol, Respectively

level	a_1	a_2	a_3	a_4	a_5	R
UB3LYP/6-31G**	−3.873	−0.025	—	—	—	0.885
	−10.561	0.074	$−0.874 \times 10^{-4}$	—	—	0.898
	−35.283	0.341	−0.001	0.111×10^{-5}	—	0.900
	293.339	−4.428	0.025	$−0.599 \times 10^{-4}$	0.538×10^{-7}	0.905
	—	—	—	—	—	0.887
UB3P86/6-31G**	−3.7591	0.02397	—	—	—	0.887
	−11.006	0.075	$−0.879 \times 10^{-4}$	—	—	0.903
	−33.412	0.309	$−0.888 \times 10^{-3}$	0.898×10^{-6}	—	0.905
	226.887	−3.338	0.018	$−0.425 \times 10^{-4}$	0.368×10^{-7}	0.908

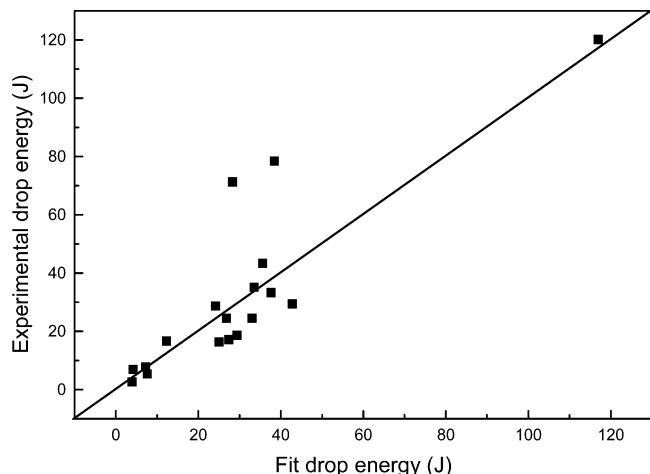


Figure 2. Comparison of fit and experimental drop energies at the UB3LYP/6-31G** level.

and 26 energetic C-nitro compounds using UB3LYP and UB3P86 methods. For C-nitro compounds the UB3LYP calculated BDE_{ZPE} is 5–12 kJ/mol less than the UB3P86 using the 6-31G** basis set, and the UB3P86 calculated BDE_{ZPE} changes slightly with the basis set varying from 6-31G** to 6-31++G**. The NBO analysis shows that chemical framework has an important influence on the energy gap between σ_{C-NO_2} and $\sigma^*_{C-NO_2}$, and it is concluded that for the model C-nitro compounds studied here the order of BDE_{ZPE} is not only in line with that of the NAO bond order but also with that of the energy gap.

When the drop energies of energetic C-nitro compounds are below 24.5 J, a good linear correlation exists between E_{dr} and BDE_{ZPE} except for the suspect LLM-119, implying that these compounds ignite by means of C–NO₂ dissociation. For the energetic C-nitro compounds that decompose through the trinitrotoluene mechanism, the impact sensitivity does not correlate with the BDE_{ZPE} , but for the energetic C-nitro compounds through the C–NO₂ dissociation mechanism the impact sensitivity is closely related to the BDE_{ZPE} indeed. Employing the UB3LYP/6-31G** calculated $BDE_{S_{ZPE}}$, a BDE_{ZPE} -based polynomial correlation of $\ln(E_{dr})$ for the 18 C–O₂ dissociation energetic compounds has been established successfully, which is also suitable for the UB3P86/6-31G** $BDE_{S_{ZPE}}$.

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