

Research Article

Predicting Heats of Explosion of Nitroaromatic Compounds through NBO Charges and ^{15}N NMR Chemical Shifts of Nitro Groups

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This work presents a new quantitative model to predict the heat of explosion of nitroaromatic compounds using the natural bond orbital (NBO) charge and ^{15}N NMR chemical shifts of the nitro groups ($^{15}\text{N}_{\text{Nitro}}$) as structural parameters. The values of the heat of explosion predicted for 21 nitroaromatic compounds using the model described here were compared with experimental data. The prediction ability of the model was assessed by the leave-one-out cross-validation method. The cross-validation results show that the model is significant and stable and that the predicted accuracy is within 0.146 MJ kg^{-1} , with an overall root mean squared error of prediction (RMSEP) below 0.183 MJ kg^{-1} . Strong correlations were observed between the heat of explosion and the charges ($R^2 = 0.9533$) and ^{15}N NMR chemical shifts ($R^2 = 0.9531$) of the studied compounds. In addition, the dependence of the heat of explosion on the presence of activating or deactivating groups of nitroaromatic explosives was analyzed. All calculations, including optimizations, NBO charges, and $^{15}\text{N}_{\text{Nitro}}$ NMR chemical shifts analyses, were performed using density functional theory (DFT) and a 6-311+G(2d,p) basis set. Based on these results, this practical quantitative model can be used as a tool in the design and development of highly energetic materials (HEM) based on nitroaromatic compounds.

1. Introduction

Aromatic molecules with nitro groups are an important class of highly energetic materials (HEM). One of the most important thermodynamic properties that determine the performance of these explosives and propellants is the heat of explosion (HE). The HE is the quantity of heat liberated when an HEM undergoes detonation as a high explosive or deflagration as a low explosive. The processes of detonation and deflagration occur even in the absence of external oxygen or air because HEM contain oxygen themselves. The HE can be theoretically calculated [1] and experimentally determined [2]. The calculated value is determined by the difference between the energies of formation of the explosive components and the energies of formation of the explosion

products. Experimentally, the HE is determined using a calorimetric bomb. The sample quantity is usually chosen to obtain a loading density of 0.1 g/cm^3 . If a powder will not explode (compounds with heat of explosion lower than 800 cal/g), a “hot” powder with a known heat of explosion is added. Thus, the HE of the sample powder can be calculated from the mixture. The calorimetric values used in this work are based on liquid H_2O as a reaction product.

Predicting the performance and thermochemical properties of energetic materials from a given molecular structure with or without using experimental measurements is critical in the research and development of explosives. Several relationships have been found that relate explosive characteristics with measured and predicted molecular properties. The relationship between thermal [3], impact [4, 5], and

electric spark [6] sensitivities and molecular structure of nitrocompounds and nitrates [7] has been the subject of many investigations. These studies concluded that the rate-determining step in the thermolysis was usually the homolytic cleavage of the C–N_{Nitro}, N–N_{Nitro}, and O–N_{Nitro} bonds. In this context, the NO₂ (nitro) functional group corresponds to the reaction center of the HEM and should be correlated with the explosive characteristics of individual energetic materials. The electron configuration and the steric conditions within the reaction center of the molecule can be represented by NMR chemical shifts of the key atoms of the center. The shifts of these atoms should correlate with characteristics of initiation reactivity of individual energetic materials [6]. The dominant factor in the initiation by shock, electric spark, and in low-temperature thermolysis should be the electronic structure and close chemical ambient of the nitrogen atom of the primary leaving nitro group. In addition, for all nitro explosives in which the R-Nitro bond is the weakest, the charge in this group (Q_{Nitro}) can be regarded as another structural parameter to assess and predict explosive properties [8]. Recently, we established a quantitative model for predicting and calculating the heat of detonation and heat of explosion for a series of nitro paraffins, nitramines [9], and nitrate esters [10] by utilizing natural bond orbital (NBO) charge analysis and the ¹⁵N NMR chemical shifts of the nitro groups. In addition, the calculated ¹⁵N_{Nitro} NMR chemical shifts for the nitramines were obtained using a protocol established in our recent work [11], which uses the continuous set of gauge transformations (CSGT) method [12]. The *ab initio* calculations of the NMR chemical shifts for different nuclei have proven to be useful structural parameters in interpreting experimental data in several applications [13, 14]. There are many both empirical and theoretical efforts to predict detonation parameters from a given molecular structure. Rice and Hare [15] introduced a computational methodology that uses only quantum mechanical (QM) information about isolated molecules to predict the heats of detonation for pure and explosive formulations. In a series of studies, Keshavarz has established simple methods for predicting heats of detonation and other explosive properties [16–19]. In the application of these methods, there is no need to use any experimental and computed data of explosives. A simple approximation is introduced for calculating heats of detonation using chemical composition of explosives and their gas phase heat of formation that can be calculated by a group additivity rule [16]. Recently, a simple method to predict heats of detonation of important classes of energetic compounds including nitroaromatics, nitramines, nitroaliphatics, and nitrate esters was introduced [17]. The methodology is based on the ratios of oxygen to carbon and hydrogen to oxygen atoms as well as the contribution of some specific functional groups or structural parameters. Previously, Keshavarz's showed that the predicted values of the heats of detonation for aromatic compounds [18] are different from those of nonaromatic compounds [1] because aromaticity can affect the values of heats of detonation. The root mean squared (rms) deviation between predicted and experimentally determined heats of detonation was

0.32 and 0.54 kJ/g for aromatic and nonaromatic energetic compounds, respectively. Also, the heats of detonation for aromatic energetic materials were estimated assuming that the heat of detonation of an explosive compound of composition C_aH_bN_cO_d can be approximated as the difference between the heat of formation of all H₂O–CO₂ arbitrary (H₂O, CO₂, N₂) detonation products and that of the explosive, divided by the formula weight of the explosive [19]. The rms deviation for this method was 0.34 kJ/g. Also, an empirical approach to calculate the heats of formation in condensed phase for different energetic compounds has been developed by Keshavarz [20]. It should be mentioned that the heat of explosion is not a constant of a high explosive and depends on the expansion ratio of the detonations products. The heat of explosion is reasonably included in the energetic characterization of the working capacity of commercial high explosives, but it has no relation to the power of brisance, which is determined by the propellant capacity. Even the detonation velocity is not a measure of the power of high explosives [21].

The purpose of this work was to establish a quantitative model to calculate and predict the heats of explosion of 35 nitroaromatic compounds from two structural parameters, nitro charges and ¹⁵N NMR chemical shifts, obtained by theoretical methods. The predictive ability of the model was assessed by the leave-one-out (LOO) cross-validation method [22]. To show the reliability of the calculated heat of explosion using the quantitative model, the results for eight nitroaromatic compounds that were not used to build the model were compared with their experimental values. The model was applied to calculate heats of explosion of twenty energetic compounds and compared against results predicted using other empirical and quantum mechanical methods and against experimental values available. In addition, the model was employed to calculate the heat of explosion of fourteen nitroaromatic compounds whose experimental values were unavailable. Importantly, this work provides a simple and rapid method for estimating heats of explosion of HEM without experimental data for a systematic set of nitroaromatic compounds and should be of help in synthesizing and developing new high explosives.

2. Experimental Section

2.1. Computational Details. Gaussian 09 [23] software was used for all theoretical calculations. Molecular geometries were optimized using the B3LYP [24, 25] functional and 6-311+G(d,p) basis set. The absolute energies and C–N_{Nitro} bond lengths for the thirty-five nitroaromatic compounds are shown in Tables 1, 2, and 3. The nitro group charges (Q_{Nitro}) were calculated according to an NBO scheme, which was implemented using Gaussian 09 software [26]. The ¹⁵N_{Nitro} NMR calculations for all tested compounds were performed using the CSGT method and are reported in Tables 1–3. NMR shifts were computed using B3LYP/6-311+G(2d,p), and the values for the ¹⁵N isotropic chemical shifts were referenced to the corresponding values for nitromethane. The effect of the solvent on the theoretical

TABLE 1: Absolute energies, code designations, $R_{C-N_{\text{Nitro}}}$ bond distances, nitro charges (Q_{Nitro}), $^{15}\text{N}_{\text{Nitro}}$ NMR calculated chemical shifts, and experimental and calculated heats of explosion for nitroaromatic compounds used to build a quantitative model.

Number	Chemical name	Code designation	Energy ^a (hartrees)	Distance $R_{C-N_{\text{Nitro}}}$ (Å)	NBO ^b charge $-Q_{\text{Nitro}}$	Calculated ^c $^{15}\text{N}_{\text{Nitro}}$ (ppm)	Experimental HE (H ₂ O liq.) (MJ kg ⁻¹)	Calculated ^d HE (MJ kg ⁻¹)
1	Tetryl	TETRYL	-1145	1.48604	0.191	-26.6	4.773	4.643
2	2,3,4,6-Tetranitroaniline	TeNA	-1105	1.47980	0.206	-25.6	4.378	4.336
3	2,4,6,2',4',6'-hexanitrodiphenylamine	HNDP	-1746	1.48079	0.210	22.8	4.075	4.099
4	Ethyl tetryl	EtTETRYL	-1185	1.48692	0.214	-23.1	4.058	4.052
5	2,4,6-Trinitrobenzoic acid	TNBA	-1035	1.48776	0.215	-23.6	3.964	4.066
6	2,4,6-Trinitrophenoxethyl nitrate	TNPHN	1280	1.48143	0.213	-21.3	3.911	3.959
7	Methyl picrate	MePi	-960	1.47516	0.222	-19.4	3.777	3.695
8	Ethyl picrate	EtPi	-999	1.47720	0.225	-19.1	3.515	3.628
9	2,4-Dinitrotoluene	24DNT	-681	1.48113	0.248	-15.7	3.192	3.043
10	2,4,6-Trinitrophenol (picric acid)	PiAc	-921	1.47425	0.228	-18.6	3.437	3.524
11	2,4,6-Trinitrocresol	TNC	-961	1.47516	0.231	-17.6	3.370	3.438
12	Dinitro- <i>ortho</i> -cresol	DN _o C	-756	1.47521	0.244	14.4	3.027	3.029
13	<i>meta</i> -Dinitrobenzene	<i>m</i> DNB	-641	1.48414	0.250	9.5	2.666	2.632
							RMSEP	0.0817

^a Calculated with B3LYP/6-311+G(d,p); ^b natural bond orbital analysis; ^c calculated with CSGT-B3LYP/6-311+G(2d,p); ^d predicted by (1).

TABLE 2: Absolute energies, code designations, $R_{C-N_{\text{Nitro}}}$ bond distances, nitro charges (Q_{Nitro}), $^{15}\text{N}_{\text{Nitro}}$ NMR calculated chemical shifts, and experimental and calculated heats of explosion for nitroaromatic compounds.

Number	Chemical name	Code designation	Energy ^a (hartrees)	Distance $R_{C-N_{\text{Nitro}}}$ (Å)	NBO ^b charge $-Q_{\text{Nitro}}$	Calculated ^c $^{15}\text{N}_{\text{Nitro}}$ (ppm)	Experimental HE (H_2O liq.) (MJ kg^{-1})	Calculated ^b HE (MJ kg^{-1})
14	1,3,5-Trinitrobenzene	TNB	-846	1.48024	0.219	-24.6	3.964	4.061
15	2,6-Dinitrotoluene	26DNT	-681	1.48266	0.240	-9.6	3.325	2.802
16	2,4,6-Trinitrotoluene	TNT	-885	1.48388	0.222	-18.9	3.766	3.665
17	2,4,6-Trinitroxyene	TNX	-925	1.48396	0.214	-12.4	3.533	3.400
18	2,4,6-Trinitroaniline	TNA	-901	1.47154	0.252	-21.3	3.589	3.318
19	2,4,6-Trinitro-1,3-dihydroxybenzene	TNR	-996	1.46312	0.243	-20.0	2.952	3.387
20	1,3,5-Trinitronaphthalene	135TNN	-999	1.48418	0.234	-15.3	3.521	3.248
21	Hexanitrostilbene	HNS	-1768	1.48668	0.205	-20.9	4.088	4.065
							RMSEP	0.284

^a Calculated with B3LYP/6-311+G(d,p); ^b natural bond orbital analysis; ^c calculated with CSGT-B3LYP/6-311+G(2d,p); ^d predicted by (1).

TABLE 3: Absolute energies, code designations, $R_{C-N_{\text{Nitro}}}$ bond distances, nitro charges (Q_{Nitro}), $^{15}\text{N}_{\text{Nitro}}$ NMR calculated chemical shifts, and predicted heats of explosion for some nitroaromatic compounds.

Number	Chemical name	Code designation	Energy ^a (hartrees)	Distance $R_{C-N_{\text{Nitro}}}$ (Å)	NBO ^b charge $-Q_{\text{Nitro}}$	Calculated ^c $^{15}\text{N}_{\text{Nitro}}$ (ppm)	Calculated ^d HE (MJ kg ⁻¹)
22	Nitrobenzene	NB	-437	1.48298	0.218	-8.7	3.109
23	<i>o</i> -Dinitrobenzene	<i>o</i> -DNB	-641	1.48063	0.207	-13.4	3.576
24	<i>p</i> -Dinitrobenzene	<i>p</i> -DNB	-641	1.48635	0.244	-19.4	3.344
25	3,5-Dinitrotoluene	35DNT	-681	1.48500	0.214	-19.3	3.393
26	1,3,5-Trimethyl-2,4,6-trinitrobenzene	TNMs	-963	1.48464	0.265	-77.0	2.276
27	1,3-Diamino-2,4,6-trinitrobenzene	DATB	-957	1.45388	0.311	-21.1	2.337
28	1,3,5-Triamino-2,4,6-trinitrobenzene	TATB	-1012	1.43669	0.390	-20.0	1.301
29	1,3,5-Trihydroxy-2,4,6-trinitrobenzene	TNPh	-1071	1.45308	0.252	-20.9	3.294
30	2-amino-4,6-dinitrophenol (picramic acid)	PicAc	-772	1.47354	0.268	-16.3	2.751
31	Dinitrochlorobenzene	CDB	-1101	1.48101	0.225	-17.6	3.537
32	1-Chloro-2,4,6-trinitrobenzene	CTB	-1306	1.48454	0.203	-20.9	4.099
33	1,3-Dichloro-2,4,6-trinitrobenzene	DCTB	-1765	1.48489	0.169	-21.7	4.698
34	1,3,5-Trichloro-2,4,6-trinitrobenzene	TCTB	-2225	1.48645	0.143	-22.6	5.188
35	Tetranitronaphthalene	TeNN	-1204	1.48469	0.217	-19.5	3.783

^a Calculated with B3LYP/6-311+G(d,p); ^b natural bond orbital analysis; ^c calculated with CSGT-B3LYP/6-311+G(2d,p); ^d predicted by (1).

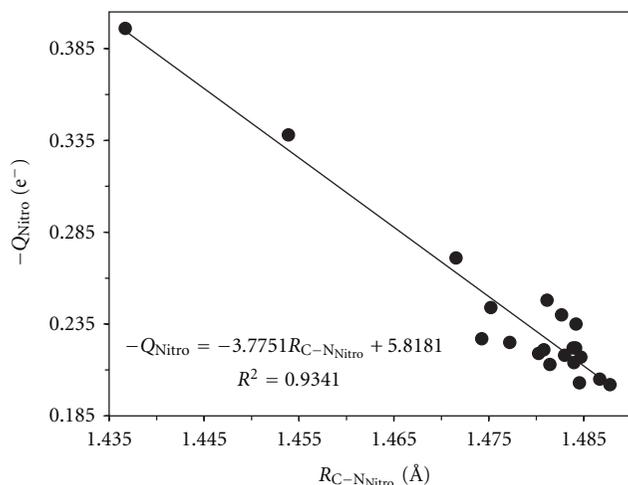


FIGURE 1: Dependence of the $R_{C-N_{\text{Nitro}}}$ bond lengths and the charges on the nitro group in nitroaromatic compounds.

NMR parameters was included using a default integral equation formalism polarized continuum model (IEF-PCM) [27] provided by the Gaussian 09 software suite. Dimethylsulfoxide (DMSO), which has a dielectric constant (ϵ) of 46.7, was used as the solvent. The experimental values of the heat of explosion used in the present paper were obtained from the literature [2].

3. Results and Discussions

3.1. Relationships between the Nitro Charges (Q_{Nitro}), the $R_{C-N_{\text{Nitro}}}$ Bond Lengths and Stability. The optimized C-N_{Nitro} bond lengths and nitro charges, with the corresponding total energies, for thirty-five nitroaromatic compounds are listed in Tables 1, 2 and 3. The charges on the nitro group (Q_{Nitro}) were calculated as the sum of the atomic charges on the nitrogen and oxygen atoms in the nitro group. It should be noted that the average values of $R_{C-N_{\text{Nitro}}}$ and Q_{Nitro} in polynitro compounds were used for all calculations, and these are listed in Tables 1–3. These results revealed that the compounds with higher stability (lower total energy) had higher nitro group charge values. Figure 1 shows a robust linear relationship ($R^2 = 0.9341$) between the $R_{C-N_{\text{Nitro}}}$ bond lengths and the nitro charges calculated with the NBO scheme.

Lower (more negative) nitro group charges were consistent with a decrease in the C-N_{Nitro} bond length. Therefore, the value of the charge on the nitro group reflects the strength of the corresponding bond and stability in these compounds. From the data shown in Tables 1–3, we concluded that the Q_{Nitro} was more sensitive to molecular changes than $R_{C-N_{\text{Nitro}}}$. For example, the $R_{C-N_{\text{Nitro}}}$ of all the isomers of dinitrobenzene (*o*, *m* and *p*) was 1.480 ± 0.006 Å; however, the Q_{Nitro} of these isomers was 0.207, 0.250, and 0.244 e⁻, respectively. In addition, the average charge on the nitro groups was increased by substituents with σ - and π -donor ability (e.g., -NH₂, -OH, -CH₃) and decreased by substituents with σ -

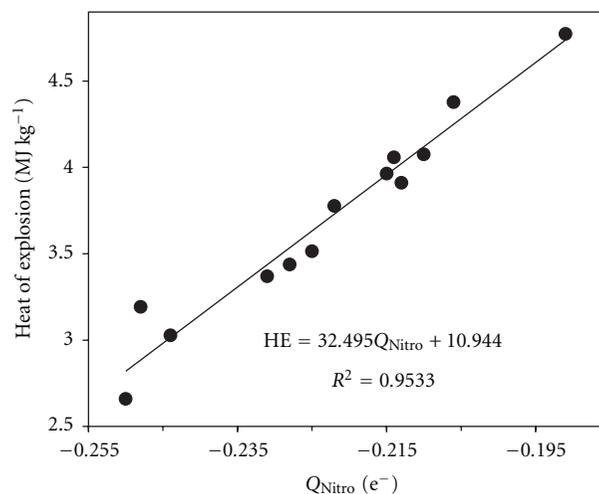


FIGURE 2: Relationship between heats of explosion and nitro charges (Q_{Nitro}) of nitroaromatic compounds.

and π -electron acceptor ability (e.g., -COOH). The Q_{Nitro} for TNA, PiAc, TNT, TNB, and TNBA was 0.252, 0.228, 0.222, 0.219 and 0.215 e⁻, respectively.

All of the $R_{C-N_{\text{Nitro}}}$ values for the studied compounds were in the range of 1.4370 to 1.4880 Å. These values were higher than the calculated $R_{C-N_{\text{Nitro}}}$ bond lengths in nitramines (1.3640–1.4021 Å) and nitrate esters (1.4180–1.4370 Å) and lower than the $R_{C-N_{\text{Nitro}}}$ bond lengths in nitro paraffins (1.5029–1.5565 Å). Our calculations showed that the introduction of amino groups into multinetrobenzene decreased the NBO nitro group charges and shortened the C-N_{Nitro} bond length. This effect was strongest when one, two or three amino groups were introduced into 1,3,5-trinitrobenzene (TNB) to form TNA, DATB, and TATB, respectively. Global analysis of the results presented above indicated that the nitro group charges can be used to assess the stability and explosive properties of this class of compounds.

3.2. NBO Nitro Charges and Heat of Explosion. The experimental heats of explosion and calculated Q_{Nitro} values obtained by the NBO scheme for 35 nitroaromatic compounds are listed in Tables 1–3. As shown in Figure 2, the relationship between the calculated Q_{Nitro} values and the experimental heat of explosion is linear, and the correlation coefficient was 0.9533, indicating that the NBO charge calculated at the B3LYP/6-311+G(d,p) level efficiently reflected the molecular environment of these compounds. The nitroaromatic compounds with higher average nitro group charges had greater experimental heat of explosion.

3.3. $^{15}\text{N}_{\text{Nitro}}$ NMR Chemical Shifts and Heat of Explosion. To find the relationship between the $^{15}\text{N}_{\text{Nitro}}$ chemical shifts of the nitro group and the heat of explosion for the nitroaromatic compounds, the isotropic ^{15}N NMR shielding tensors were investigated theoretically at the B3LYP/6-311+G(2d,p) level within the CSGT model. In our recent work, a strong

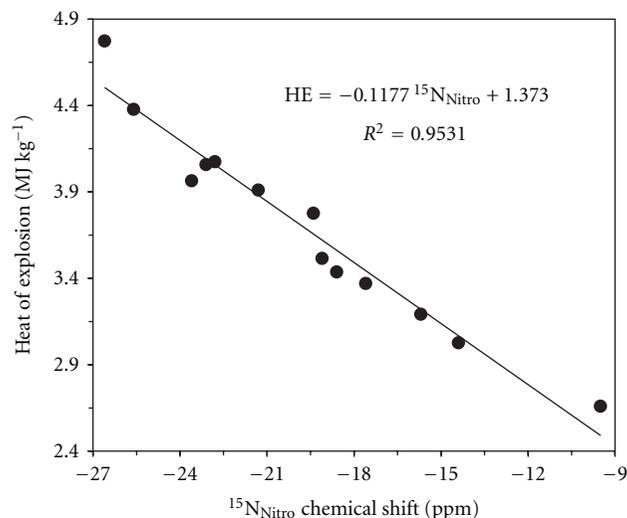


FIGURE 3: Relationship between heats of explosion and $^{15}\text{N}_{\text{Nitro}}$ NMR chemical shifts for nitroaromatic compounds.

correlation was found between the heat of detonation and heat of explosion for nitramines, nitro paraffins, and nitrate esters and the corresponding $^{15}\text{N}_{\text{Nitro}}$ chemical shifts. Zeman's work is noteworthy for its correlation between explosive properties (impact and electric sparks sensitivities, detonation, and thermal decomposition) and the ^{13}C and $^{15}\text{N}_{\text{Nitro}}$ NMR chemical shifts of polynitro compounds [28]. The $^{15}\text{N}_{\text{Nitro}}$ NMR chemical shift results for the 35 nitroaromatic studied are listed in Tables 1–3. The correlation between heat of explosion and the calculated $^{15}\text{N}_{\text{Nitro}}$ chemical shifts is shown in Figure 3. As seen in this figure, the heat of explosion increased with a decreasing $^{15}\text{N}_{\text{Nitro}}$ chemical shift. The regression coefficient (R^2) obtained for the correlation between the heat of explosion and $^{15}\text{N}_{\text{Nitro}}$ chemical shifts was 0.9531. Although NMR studies in solution neglect important crystal-lattice interactions affecting some explosive properties, this particular correlation provided a consistent method for the assessment of the heat of detonation without the use of experimental data for a systematic set of nitroaromatic compounds.

3.4. Quantitative Relationships between the Heat of Explosion (HE), Q_{Nitro} and $^{15}\text{N}_{\text{Nitro}}$ NMR Chemical Shifts. To verify the relationship between the two parameters described in the previous section (Q_{Nitro} and $^{15}\text{N}_{\text{Nitro}}$) and the heat of explosion, 13 nitroaromatic compounds, each with a heat of explosion that had been measured experimentally, were correlated with our calculated values. These were obtained from the theoretical structural parameters (listed in Table 1). The following equation was determined from the linear regression fit:

$$\text{HE} = 16.423 \times (Q_{\text{Nitro}}) - 0.06 \times (^{15}\text{N}_{\text{Nitro}}) - 6.15. \quad (1)$$

The significance of the results can be evaluated by the results of the statistical parameters $R^2 = 0.9782$, $\text{SE} = 0.093$,

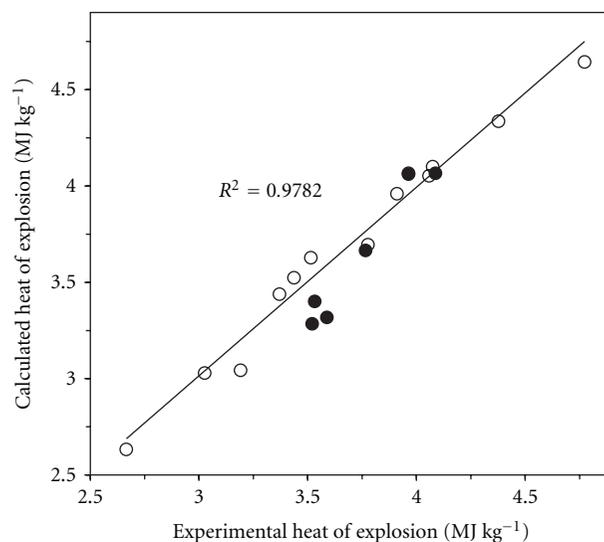


FIGURE 4: Correlation between calculated and experimental heats of explosion for nitroaromatic compounds. Molecules used to build a quantitative model (○) and other nitroaromatic compounds (●).

and $\text{RMSEP} = 0.0817 \text{ MJ kg}^{-1}$, where R^2 , SE, and RMSEP are the correlation coefficient, the standard error, and the root mean squared error prediction, respectively. As seen from (1), a nitroaromatic explosive with a large average Q_{Nitro} value and a low $^{15}\text{N}_{\text{Nitro}}$ chemical shift has a high heat of explosion. The stability and prediction capability of the quantitative model established by (1) was assessed using the leave-one-out (LOO) cross-validation method. In the LOO method procedure, one explosive is removed from the training set (the explosives are listed in Table 1), and a model is developed with remaining $N-1$ explosives. At each step, the heat of explosion value of the removed explosive is predicted. This process was repeated until each molecule of the training set is predicted. The prediction capability of the model was quantified in terms of r_{cv} and S_{cv} , which are defined as follows:

$$r_{\text{cv}}^2 = 1.0 - \frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{\sum_{i=1}^n (y_i - \bar{y})^2}, \quad (2)$$

$$S_{\text{cv}} = \sqrt{\frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{N - D - 1}},$$

where y_i and \hat{y}_i are the experimental and predictive values, respectively, \bar{y} is the mean value of y_i , N is the number of explosives to be used for building the model, and D is the number of descriptors in the model. The r_{cv} and S_{cv} values were 0.9727 and 0.146, respectively, which indicated that (1) was reasonably stable. The predicted accuracy of (1) for the heat of explosion of the nitroaromatic compounds was within 0.146 MJ kg^{-1} . Figure 4 shows a comparison between the experimental heat of explosion, as predicted by (1), and the corresponding regression coefficient for the nitroaromatic compounds. The calculated heats of explosion

TABLE 4: Comparison of calculated heats of explosion, for nitroaromatic compounds, according to (1), HE_{R-H} [15], HE_{MHK1} [18], and HE_{MHK2} [17] method with experimental values [2].

Code designation	Experimental HE (H ₂ O liq.) (MJ kg ⁻¹)	HE_{R-H} (H ₂ O liq.) (K-J, t) ^a	HE_{R-H} (H ₂ O liq.) (MJ kg ⁻¹) (K-J, e) ^b	(K-J)mod., e) ^c	HE_{MHK2} (MJ kg ⁻¹)	HE_{MHK1} (MJ kg ⁻¹)	Calculated HE (MJ kg ⁻¹)
Tetryl	4.773	5.318	6.234	4.740	4.118	4.205	4.643
TeNA	4.378	5.485	6.138	4.912	4.245	4.594	4.336
TNB	3.964	5.067	5.845	4.711	3.617	4.109	4.061
24DNT	3.192	3.795	5.322	3.740	3.225	2.959	3.043
26DNT	3.325	3.908	5.435	3.845	3.225	2.959	2.802
TNT	3.766	4.694	5.795	4.259	3.546	3.725	3.665
TNA	3.589	4.656	5.565	4.368	3.822	4.004	3.318
PiAc	3.437	4.853	5.602	4.305	3.751	3.321	3.524
<i>m</i> DNB	2.666	4.289	5.443	3.870	3.228	3.388	2.632
HNS	4.088	5.017	5.749	4.284	4.027	3.934	4.065
RMSEP		1.046	2.023	0.671	0.332	0.362	0.204

^a Heat of detonation calculated using Kamlet-Jacobs method. The t denotes that the values used for the heats of formation for the products are predicted. ^bThe e denotes that the values used for the heats of formation for the products are the experimental values. ^cModified Kamlet and Jacobs method.

TABLE 5: Comparison of calculated heats of explosion for nitrate esters according to HE_{I-H} [10] and HE_{MHK2} method [17] with experimental values [2].

Chemical name	Experimental HE (H_2O liq.) ($MJ\ kg^{-1}$)	HE_{MHK2} ($MJ\ kg^{-1}$)	HE_{I-H} ($MJ\ kg^{-1}$)
Erythritol tetranitrate	6.356	6.555	6.362
Glycerol trinitrate	6.671	6.520	6.847
n-propyl nitrate	3.272	2.963	3.377
Isopropyl nitrate	3.126	2.963	3.106
Diethylene glycol dinitrate	4.566	4.624	4.389
Dioxiethylnitramine dinitrate	5.458	5.019	5.307
Dipentaerythritol hexanitrate	5.143	4.995	5.523
Butanetriol trinitrate	6.022	5.464	5.824
Metriol trinitrate	4.945	4.774	5.202
Pentaerythritol tetranitrate	6.322	5.717	6.316
	RMSEP	0.333	0.186

values were very similar to the values obtained in the experiments. These results validate our new method for calculating heat of explosion using the NBO charges on and ^{15}N NMR chemical shifts of nitro groups as structural parameters.

3.5. Predicting the Heat of Explosion for Nitroaromatic Explosives. The predicted detonation heat by (1) for 14 nitroaromatic explosives with unmeasured HEs is given in Table 3. Based on the HE predictions for the halogen derivatives of nitrobenzene, the HE had the following trend: CDB < CTB < DCTB < TCTB. Nitroaromatic compounds with a higher number of halogen atoms exhibit a higher heat of explosion. However, this theoretical study was carried out in solution neglect important crystal-lattice effects that are important in the determination of explosive properties. Zeman's work [29] established an inverse relationship between the volatility and Chapman-Jouguet (C-J) pressure. The increased volatility due to multiple substitution is linked with the deformation of the molecules that accompany the substitution. Therefore, it is of utmost importance the intermolecular nonbonding interaction. Global analysis of the results presented in Tables 1–3 indicated that the HE values of 2,4,6-trinitrobenzene derivatives decreased systematically with the number of activating groups in the molecular structure of the nitroaromatic explosive. The HE trend for the halogenated nitrobenzenes agreed with the σ - and π -donor ability of the compounds. In addition, the heat of explosion for 2,4,6-trinitrobenzene monosubstituted derivatives increased with substituents that had a larger σ - and π -electron acceptor ability, which was consistent with smaller nitro group charges and $^{15}N_{Nitro}$ chemical shifts.

3.6. Comparison of the Calculated Heats of Explosion with Other Empirical and Quantum Mechanical Methods. The heats of explosion for various nitro-aromatic and nitrate esters are given in Tables 4 and 5 and compared with experimental values, two empirical methods (KHM1 [18] and KHM2 [17]) and Rice-Hare methods [15]. Predicted heats of explosion for $H_2O_{(l)}$ using quantum mechanical approach including predicted and experimental values for

the heat of formation have RMSEP from experiment of 1.046 and 2.023 $MJ\ kg^{-1}$, respectively, whereas the modified version of Kamlet-Jacobs's method results has a substantially lower deviation from experiment (0.671 $MJ\ kg^{-1}$). As shown in Table 4, the RMSEP of empirical methods (0.332 and 0.362 $MJ\ kg^{-1}$) are lower than the quantum mechanical methods. As indicated in Tables 4 and 5, the predicted heats of explosion calculated by the new model deviated from experiment by less than 0.204 $MJ\ kg^{-1}$. As is evident, the proposed model based on the calculation of two structural parameters shows the best agreement with experimental data.

This method for predicting the heat of explosion of nitroaromatic explosives, that is, using NBO charges and ^{15}N NMR chemical shifts as references, can be generalized for other homologous systems if these parameters are calculated with the same computational approach. Hence, the computation of the heat of explosion equation will be useful in the design and development of strong nitroaromatic explosives when experimental data are not available. However, the heat of explosion depends on many factors besides nitro group charges or $^{15}N_{Nitro}$ NMR chemical shifts; a completely monotonic correlation between these factors was not found, which indicates that this quantitative model is only applicable to the nitroaromatic explosives whose stabilities are determined by the chemical bonds linked to the nitro group. Based on the previous discussion, it can be concluded that a consistent correlation between the heat of explosion and the Q_{Nitro} and $^{15}N_{Nitro}$ chemical shifts exists in such explosives.

4. Conclusion

NBO charge and ^{15}N NMR chemical shift analyses are two key parameters that can be used to determine the heat of explosion of aromatic explosives. Using these two structural parameters, a good quantitative model was established for predicting the heat of explosion of 35 nitroaromatic explosives. The model was significant and stable and displayed prediction accuracy within 0.146 $MJ\ kg^{-1}$, with an overall root mean squared error of prediction (RMSEP) below

0.183 MJ kg⁻¹. The heat of explosion of nitroaromatic compounds decreased systematically with the type and number of activating substituents (σ - and π -donors) and increased with the number of σ - and π -electron acceptors added to the corresponding molecular structure. Based on these results, the proposed model could be used to predict the heat of explosion without experimental data for a systematic set of nitroaromatic compounds and could aid in the design of these highly energetic materials. The calculated heats of explosion by this model give better results than other empirical and quantum mechanical methods available in the literature.

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