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A reliable method for prediction of enthalpy of fusion in energetic materials using their molecular structures

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Abstract

A new method is introduced to predict the enthalpy of fusion of energetic materials, which can undergo very rapid and highly exothermic reactions. It can be applied for different classes of energetic compounds including polynitro arenes, polynitro heteroarenes, acyclic and cyclic nitramines, nitrate esters, nitroaliphatics, cyclic and acyclic peroxides as well as nitrogen rich compounds. This model is based on linear combination of elemental composition as additive part and two correcting functions as non-additive contributions, which depend on intermolecular interactions. It can be easily applied for energetic compounds containing complex molecular structure. For 194 different energetic compounds (corresponding to 233 measured values), the predicted results of this simple model, on the basis of additive contribution and correcting functions, give more reliable results as compared to two of the best available predictive methods.

Keywords: Enthalpy of fusion; Energetic material; Molecular structure; Correlation

List of Symbols

$\Delta_{fus}H$	Enthalpy of fusion (kJ mol^{-1})
$(\Delta_{fus}H)_{add}$	Additive contribution of the enthalpy of fusion (kJ mol^{-1})
$(\Delta_{fus}H)_{non-add}^{inc}$	Non-additive contribution of the increasing parameters in enthalpy of fusion (kJ mol^{-1})
$(\Delta_{fus}H)_{non-add}^{dec}$	Non-additive contribution of the decreasing parameters in enthalpy of fusion (kJ mol^{-1})
$\Delta_{fus}S$	Entropy of fusion (kJ mol^{-1})
T_{fus}	Fusion temperature (K)
n_C	Number of carbon atoms
n_H	Number of hydrogen atoms
n_N	Number of nitrogen atoms
$n_{O(S)}$	Number of oxygen (or sulfur) atoms
n_{hal}	Number of halogen atoms

1. Introduction

Due to non-ideal behaviors of energetic materials and unavailability of experimental thermophysical data for many of energetic materials, it is important to develop reliable predictive methods to eliminate poor candidates from further consideration. However, suitable predictive methods are essential before expensive and often hazardous synthesis and testing processes of new high energy materials. For safe handling, storage and process design of a new energetic material, it is essential to have thermochemical properties. Different methods have been developed to predict thermodynamic and physical properties of energetic compounds as well as their sensitivity with respect to different stimuli [1-7].

Thermal analysis of energetic compounds reveals that they can start to decompose at certain temperature. Their exothermic chemical reaction overcomes the ability of the explosive charge to dissipate the applied heat [8]. Decomposition initiates usually above or during the melting process. However, energetic materials with higher melting points have high thermal stability. For example, the introduction of the amino groups in nitroaromatics can raise their melting points and thermal stabilities [9, 10]. For polynitroaromatics, large molecular masses and better molecular symmetries are also responsible for high melting point and favorable thermal stability [10]. Furthermore, it was found that decomposition of polynitroaromatics is more rapid in molten phase [11].

Enthalpy of fusion ($\Delta_{fus}H$), which is defined as the enthalpy change in the transition from the most stable form of solid to liquid state of high energy compounds. It can be related to the entropy of fusion ($\Delta_{fus}S$) and the fusion temperature (T_{fus}), i.e. $\Delta_{fus}H = T_{fus} \Delta_{fus}S$. Zeman and coworkers [12-15] were stabilized some relationships

between $\Delta_{fus}H$ and impact sensitivity as well as electric spark sensitivity of nitramines and polynitro compounds. Differential scanning calorimetry (DSC) can be used for measuring $\Delta_{fus}H$ of explosive materials [16]. For some of the explosives, which can be decomposed in solid phase, $\Delta_{fus}H$ should be predicted. Moreover, prediction of $\Delta_{fus}H$ creates a better insight about the intermolecular interactions and sensitivity of energetic molecules, which have not been synthesized yet.

Quantitative structure–property relationships (QSPR) [17], quantum mechanics [18], group contribution method [19, 20], artificial neural network [21] and simple correlations on the basis of molecular structures [22-27] are suitable methods for predicting $\Delta_{fus}H$. QSPR methods require special computer codes and their training set should contain large number of compounds with different molecular structures to obtain suitable results for the compounds with similar molecular structure in test set. Moreover, they are based on complex molecular descriptors, which are difficult to understand and interpret their effects. They were often used to predict thermodynamic properties of particular chemical families of compounds [28]. The group contribution methods have also been developed to predict the values of $\Delta_{fus}H$ for different types of organic compounds [29-33]. They may give large deviations in $\Delta_{fus}H$ for some organic energetic compounds [17, 34]. For several energetic compounds, quantum mechanical methods have been used to study their phase change properties [18, 35, 36]. These methods require high speed computers and specific computer codes. Some simple methods have also been developed on the basis of molecular structures for prediction of the values of $\Delta_{fus}H$ for some classes of energetic compounds [22-26]. Since these correlations are restricted to certain classes of energetic compounds, application of certain correlation belong to one class of energetic compounds to the other classes may

lead to large deviations. The purpose of this work is to improve previous correlations [22-26] in order to introduce a general and simple approach for prediction of the values of $\Delta_{fus}H$ in large classes of energetic compounds including polynitro arene, polynitro heteroarene, acyclic and cyclic nitramine, nitrate ester, nitroaliphatic, cyclic and acyclic peroxides as well as nitrogen rich compounds. It will be shown that the new method is based on elemental composition and two correcting functions as increasing and decreasing contribution terms. The values of correcting functions depend on attractions and repulsions resulting from different molecular moieties. This method can also be applied to halogenated energetic materials as well as energetic materials containing complex molecular structures.

2. Materials and method

2.1. Additive contribution of elements

There are a large variety of steric, inter- and intra-molecular interactions due to the contribution of dipole moment, polarizability, hydrogen bond donor and acceptors. There are some additive and non-additive constitutive properties for T_{fus} [37-41] and $\Delta_{fus}S$ [42] of energetic compounds. For some classes of the energetic compounds with the general formula $C_aH_bN_c(O \text{ or } S)_d(\text{halogen})_e$, it was shown that the elemental composition can be used as an essential parameter for prediction of their $\Delta_{fus}H$ [22, 27]. The study of $\Delta_{fus}H$ for the other classes of energetic compounds, including cyclic and acyclic peroxides and nitrogen rich compounds as well as energetic compounds containing complex molecular structures and simultaneously multiple different energetic bonds such as N-NO₂ and C-NO₂, has shown that the contribution of

elemental composition is also important for these compounds. However, previous model has been extended for large classes of energetic compounds where their experimental data for 194 energetic compounds (corresponding to 233 experimental data) are given in Table 1. Molecular structures of these compounds are also given in Table S.1 as supporting information. The additive contribution of elemental composition in $\Delta_{fus}H$ can be derived on the basis of experimental data using multiple linear regression as:

$$\left(\Delta_{fus}H\right)_{add} = 0.6047 n_C + 0.6211 n_H + 2.750 n_N + 1.424 n_{O(S)} + 3.048 n_{hal} \quad (1)$$

where $\left(\Delta_{fus}H\right)_{add}$ is the additive contribution of elemental composition in kJ mol^{-1} ; n_C , n_H , n_N , $n_{O(S)}$ and n_{hal} are the number of carbon, hydrogen, nitrogen, oxygen (or sulfur) and halogen atoms, respectively. As indicated in Eq. (1), all coefficients of elemental composition have positive sign, which confirms positive contribution of elemental composition.

2.2. Non-additive contribution

With respect to the existence of some specific polar groups and molecular fragments, some non-additive corrections can be used to adjust the predicted $\left(\Delta_{fus}H\right)_{add}$. Based on additive and non-additive contributions, using multiple linear regression, the optimized correlation is given as Eq. (2):

$$\Delta_{fus}H = 0.9781\left(\Delta_{fus}H\right)_{add} + 7.567\left(\Delta_{fus}H\right)_{Non-add}^{Inc} - 8.784\left(\Delta_{fus}H\right)_{Non-add}^{Dec} \quad (2)$$

where $\left(\Delta_{fus}H\right)_{Non-add}^{Inc}$ and $\left(\Delta_{fus}H\right)_{Non-add}^{Dec}$ are non-additive contributions for increasing and decreasing effects of specific groups on $\Delta_{fus}H$.

3. Results and discussion

The values of $\Delta_{fus}H$ are affected by intermolecular interactions, for example, the values of $\Delta_{fus}H$ of benzene, aniline, and phenol are 9.87, 10.54, 11.51 kJ mol⁻¹, respectively [43] which means that adding the polar groups to a molecule, increase its $\Delta_{fus}H$. As another example, the values of $\Delta_{fus}H$ of 2-nitroaniline, 3-nitroaniline, and 4-nitroaniline are 16.11, 23.68, 21.09 kJ mol⁻¹, respectively [43] which shows that intramolecular hydrogen bonding in 2-nitroaniline is responsible of its lower $\Delta_{fus}H$. As a general rule, intermolecular attractions of a molecule with its neighboring molecules will be increased by the presence of polar groups. In contrast, intramolecular attractions will be decreased in the presence of intramolecular hydrogen bonding. However, the existence of polar groups, such as -OH, -COOH, -NH₂, and intramolecular attractions in $\Delta_{fus}H$ can be contributed as non-additive terms. Table 2 contains some functional groups and molecular fragments, which can be used to determine the values of

$$\left(\Delta_{fus}H\right)_{Non-add}^{Inc} \text{ and } \left(\Delta_{fus}H\right)_{Non-add}^{Dec}.$$

3.1. Contribution of some of polar groups and molecular fragments in $\left(\Delta_{fus}H\right)_{Non-add}^{Inc}$

- 1) **-OH and -COOH groups in aromatic compounds:** The value of

$\left(\Delta_{fus}H\right)_{Non-add}^{Inc}$ is 0.7, except -OH group between two nitro groups in an aromatic

structure in which the value of $\left(\Delta_{fus}H\right)_{Non-add}^{Inc}$ is zero.

- 2) **-NH₂ group:** The value of $\left(\Delta_{fus}H\right)_{Non-add}^{Inc}$ for the existence of one or two amino

groups, in both aromatics and non-aromatics, is 0.5. For the attachment of more

than two amino groups in aromatic rings, $(\Delta_{fus}H)_{Non-add}^{Inc}$ is 2.6. Meanwhile for mononitro derivatives, if the nitro group exists in ortho position to amino group,

$(\Delta_{fus}H)_{Non-add}^{Inc}$ is zero.

- 3) **>NH group:** For the presence of >NH fragment, $(\Delta_{fus}H)_{Non-add}^{Inc}$ is 0.5.
- 4) **>N-NO₂ group in acyclic nitramines:** For more than three >N-NO₂ groups, $(\Delta_{fus}H)_{Non-add}^{Inc}$ is equal to $(n_{NNO_2}-2)$ where n_{NNO_2} is the number of >N-NO₂ groups in acyclic nitramines.
- 5) **-N(C=O)N- group:** For the existence of this polar group, the value of $(\Delta_{fus}H)_{Non-add}^{Inc}$ is 1.5.

3.2. Contribution of structural moieties in the $(\Delta_{fus}H)_{Non-add}^{Dec}$

- 1) **Ar-X-Ar nitroaromatics:** Planarity and the packing efficiency of these molecules in the crystals will be reduced [31]. Thus, the experimental enthalpies of fusion will be decreased here. In these cases, the value of $(\Delta_{fus}H)_{Non-add}^{Dec}$ is 0.5, except for the Ar-S-Ar structures which is zero.
- 2) **Cyclic nitramines:** For cyclic nitramines containing more than six-membered ring containing only carbon and nitrogen atoms ($m_{cyc} > 6$), $(\Delta_{fus}H)_{Non-add}^{Dec} = \frac{m_{cyc} - 6}{4} + 0.5$.
- 3) **-NO₂ group in non-aromatic compounds:** The value of $(\Delta_{fus}H)_{Non-add}^{Dec}$ is equal to 1.0 for the presence of nitro groups in acyclic and cyclic alkanes.

- 4) **–N–N=O group:** For the existence of nitroso group, $\left(\Delta_{fus}H\right)_{Non-add}^{Dec}$ is 2.0.

If the above conditions are not satisfied, both correcting functions are zero.

3.3. The reliability of the new model

A graphical comparison between Jain et al. [30], Mosaei Oskoei-Keshavarz [22] and new method, i.e. Eq. (2), has been showed in Fig. 1. As shown in Fig. 1, scattering of results of the new method is lower than other predictive methods.

Coefficient of determinations [44], R^2 , determines that if regression accounts for the variation or not. $R^2=1.0$ means that the regression accounts for all of the variations. Due to the presence of various steric effects, inter- and intra- molecular interactions as well as the uncertainty in the experimental values of heats of fusion, the coefficient of determinations are relatively good, i.e. $R^2= 0.85$ and 0.88 in Eqs. (1) and (2), respectively. This situation is consistent with large difference between experimental values from various sources; for example in the case of TNT different values of heats of fusion, from 19.50 [13] to 24.7 kJ mol^{-1} [43], were reported. As shown in Table 1, the predicted $\Delta_{fus}H$ by Eq. (2) for 194 energetic compounds containing complex molecular structures, are in good agreement with the experimental data. As also indicated in Table 1, the predicted results were compared with two of the best available empirical methods, i.e. Jain et al. [30] and Mosaei Oskoei-Keshavarz [22] methods. It should be noted here, as shown in Table 1, the method of Jain et al. [30] cannot be applied for some of the energetic compounds such as guanidine nitrate and 4,6-dinitrobenzofurazan 1-oxide because some of group contributions for their molecular fragments are not defined. Comparisons of the predicted results of Eqs. (1) and (2) with respect to Jain et al. [30] and Mosaei Oskoei-Keshavarz [22] methods are given in Table 1 for different classes of

energetic compounds including acyclic nitramines, cyclic nitramines, nitrate esters, polynitro arenes, polynitro heteroarenes, nitroaliphatics, nitroaromatics, cyclic peroxides, acyclic peroxides and nitrogen rich compounds. Average values of deviation ($\overline{\text{Dev.}}$) and enthalpy of fusion ($\overline{\Delta H_{\text{fus}}}$) have been added at the end of each categories of energetic materials in Table 1. It can be expected that Eq. (1) shows high deviations for those compounds containing special polar groups and molecular moieties corresponding to $\left(\Delta_{\text{fus}} H\right)_{\text{Non-add}}^{\text{Inc}}$ and $\left(\Delta_{\text{fus}} H\right)_{\text{Non-add}}^{\text{Dec}}$ with respect to Eq. (2). As seen in Table 1, Eq. (1) and Eq. (2) have the highest deviations for 2,4,6,8,10,12-tetranitro-2,4,6,8,10,12-hexaazatridecane (44.81 kJ/mol) and 1,3-dinitro-1,3-diazacyclohexane (-20.63 kJ/mol), respectively. Meanwhile, Eq. (1) and Eq. (2) give the lowest deviations for ethylene oxide (0.05 kJ/mol) and benzidine (-0.06 kJ/mol), respectively. Table 3 summarizes average deviations with all methods per family of compounds. The proposed models were applied for energetic compounds in ten different categories listed in Table 3.

Assessing the predictive ability of new models has been done by some statistical parameters as shown in Table 4 for Eqs. (1) and (2) as well as for the models of Ref [30]. and Ref. [22]. These parameters includes a) Mean Error, ME, b) Root Mean Squared deviation, RMS, c) Mean Absolute Error, MAE, d) Mean Absolute Percent Error, MAPE, and e) Maximum of errors. Definition and the importance of each of these parameters were given elsewhere [45]. According to statistical parameters given in Table 4, the suggested models were validated and approved through the lowest errors. ME is a measure of accuracy and defines the value of bias. Eqs. (1) and (2) have ME equal to 0.43 and 0.20 kJ mol⁻¹, respectively. Thus, both new models are accurate, unbiased, and free from systematic errors. RMS is a measure of precision. It can be used to determine the spreading of data around the regression model. RMS values of Eqs. (1)

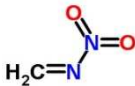
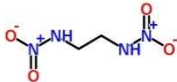
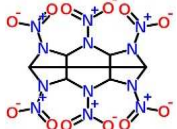


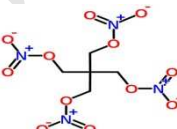
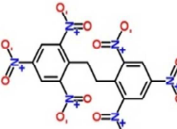
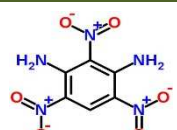

and (2) from experiment are 8.72 and 6.03 kJ mol⁻¹, respectively. The RMS value of Mosaei Oskoei-Keshavarz [22] method is 8.92 kJ mol⁻¹, which is higher than both Eqs. (1) and (2). Also, Jain et al. [30] method gives highest RMS value (9.88 kJ mol⁻¹) because their model is a general method in which few energetic compounds were used to develop this method. This comparison confirms that Eqs. (1) and (2) have high reliability and precision. MAE is another measure of errors which determines the average error when negative signs are ignored. For a Gaussian distribution of errors, the ratio of RMS to MAE is near 1.25 [46]. On the basis of Table 4, this ratio is 1.39 for Eq. (1) and 1.35 for Eq. (2). Therefore, the error distributions in the new models are almost normal. Moreover, maximum of errors, which determines the worst error in the predictions, is a measure of precision. Three statistical parameters RMS, MAE and maximum of errors confirm that the reliability of Eq. (1), which is based on only elemental composition, is higher than general method of Jain et al. [30]. Thus, Eq. (1) can be used for the other classes of organic compounds but its reliability is low because non-additive correction factors should be considered for strong attractions between functional groups, e.g. hydrogen bonding. Although maximum error and MAE of Eq. (1) is higher than Mosaei Oskoei-Keshavarz [22] method but RMS and ME of Eq. (1) is lower than the method of Mosaei Oskoei-Keshavarz [22]. High reliability of Eq. (2) as compared to Eq. (1) confirms that it is essential to consider inter- and intra- molecular interactions as non-additive parameters beside only elemental composition given in Eq. (1) for prediction of $\Delta_{fus}H$. All of these reasons reveal that the new models, especially Eq. (2), are free from systematic errors and can predicts heats of fusion with sufficient accuracy and precision. Some examples of application of Eq. (2) for different classes of energetic compounds are given in Appendix.

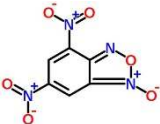
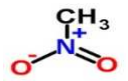
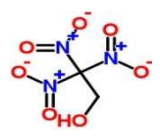
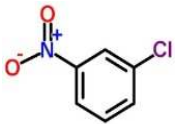
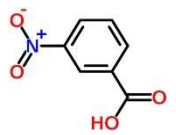
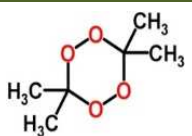
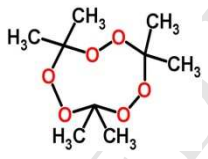
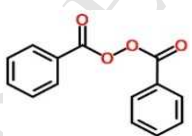
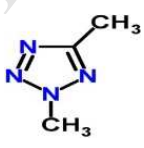
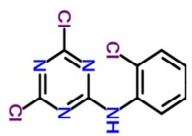
4. Conclusions

A simple method was introduced for prediction of the values of $\Delta_{fus}H$ in acyclic and cyclic nitramines, nitrate esters, polynitro arenes, polynitro heteroarenes, nitroaliphatics, cyclic and acyclic peroxides as well as nitrogen rich compounds such as triazoles, tetrazoles. Eq. (1) is based on elemental composition of energetic material, which can be found by chemical formula. Eq. (2) considers non additive functions on the basis of some molecular fragments and functional groups, which can be defined using the structure of energetic molecule. Thus, the present method gives the simplest and easiest procedure and at the same time gives reliable results with respect to the other available methods.

Appendix

Some examples of application of Eq. (2) for different classes of energetic compounds including acyclic nitramines, cyclic nitramines, nitrate esters, polynitro arenes, polynitro heteroarenes, nitroaliphatics, nitroaromatics, cyclic peroxides, acyclic peroxides and nitrogen rich compounds

Class of compound	Name	Molecular structure	The calculated $\Delta_{fus}H$ by Eq. (2)
Acyclic Nitramine	N-Nitromethanimine (DIGEN)		$\Delta_{fus}H=0.9781[0.6047(1)+0.6211(2)+2.750(2)+1.424(2)+3.048(0)]+7.567(0)-8.784(0)=9.97 \text{ kJ/mol}$
	N,N'-Dinitroethylenediamine (EDNA)		$\Delta_{fus}H=0.9781[0.6047(2)+0.6211(6)+2.750(4)+1.424(4)+3.048(0)]+7.567(0.5)-8.784(0)=24.94 \text{ kJ/mol}$
Cyclic Nitramine	2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20)		$\Delta_{fus}H=0.9781[0.6047(6)+0.6211(6)+2.750(12)+1.424(12)+3.048(0)]+7.567(0)-8.784(0)=56.18 \text{ kJ/mol}$
	1,3,5,7-Tetranitro-1,3,5,7-tetrazocane (HMX)		$\Delta_{fus}H=0.9781[0.6047(4)+0.6211(8)+2.750(8)+1.424(8)+3.048(0)]+7.567(0)-8.784(1)=31.10 \text{ kJ/mol}$
Nitrate Ester	Diethyleneglycol dinitrate		$\Delta_{fus}H=0.9781[0.6047(4)+0.6211(8)+2.750(2)+1.424(7)+3.048(0)]+7.567(0)-8.784(0)=22.35 \text{ kJ/mol}$
	Pentaerythritol Tetranitrate (PETN)		$\Delta_{fus}H=0.9781[0.6047(5)+0.6211(8)+2.750(4)+1.424(12)+3.048(0)]+7.567(0)-8.784(0)=35.29 \text{ kJ/mol}$
Polynitro Arene	1,2-Bis(2,4,6-trinitrophenyl)ethane (DPE)		$\Delta_{fus}H=0.9781[0.6047(14)+0.6211(8)+2.750(6)+1.424(12)+3.048(0)]+7.567(0)-8.784(0.5)=45.99-4.39=41.60 \text{ kJ/mol}$
	1,3-Diamino-2,4,6-trinitrobenzene (DATB)		$\Delta_{fus}H=0.9781[0.6047(6)+0.6211(5)+2.750(5)+1.424(6)+3.048(0)]+7.567(0.5)-8.784(0)=32.17 \text{ kJ/mol}$
Polynitro heteroarene	2,4,6-Trinitropyridine		$\Delta_{fus}H=0.9781[0.6047(5)+0.6211(2)+2.750(4)+1.424(6)+3.048(0)]+7.567(0)-8.784(0)=23.29 \text{ kJ/mol}$

Nitroaliphatic	4,6-Dinitrobenzofurazan 1-oxide		$\Delta_{\text{fus}}H = 0.9781[0.6047(6) + 0.6211(2) + 2.750(4) + 1.424(6) + 3.048(0)] + 7.567(0) - 8.784(0) = 23.88 \text{ kJ/mol}$
	Nitromethane		$\Delta_{\text{fus}}H = 0.9781[0.6047(1) + 0.6211(3) + 2.750(1) + 1.424(2) + 3.048(0)] + 7.567(0) - 8.784(0) = 7.89 \text{ kJ/mol}$
Nitroaromatic	2,2,2-Trinitroethanol		$\Delta_{\text{fus}}H = 0.9781[0.6047(2) + 0.6211(3) + 2.750(3) + 1.424(7) + 3.048(0)] + 7.567(0) - 8.784(1) = 12.04 \text{ kJ/mol}$
	1-Chloro-3-nitrobenzene		$\Delta_{\text{fus}}H = 0.9781[0.6047(6) + 0.6211(4) + 2.750(1) + 1.424(2) + 3.048(1)] + 7.567(0) - 8.784(0) = 14.43 \text{ kJ/mol}$
Cyclic peroxide	3-Nitrobenzoic acid		$\Delta_{\text{fus}}H = 0.9781[0.6047(7) + 0.6211(5) + 2.750(1) + 1.424(4) + 3.048(0)] + 7.567(0.7) - 8.784(0) = 20.73 \text{ kJ/mol}$
	3,3,6,6-Tetramethyl-1,2,4,5-tetraoxane (DADP)		$\Delta_{\text{fus}}H = 0.9781[0.6047(6) + 0.6211(12) + 2.750(0) + 1.424(4) + 3.048(0)] + 7.567(0) - 8.784(0) = 16.41 \text{ kJ/mol}$
Acyclic peroxide	3,3,6,6,9,9-Hexamethyl-1,2,4,5,7,8-hexaoxonane		$\Delta_{\text{fus}}H = 0.9781[0.6047(9) + 0.6211(18) + 2.750(0) + 1.424(6) + 3.048(0)] + 7.567(0) - 8.784(0) = 24.61 \text{ kJ/mol}$
	Benzoyl peroxide		$\Delta_{\text{fus}}H = 0.9781[0.6047(14) + 0.6211(10) + 2.750(0) + 1.424(4) + 3.048(0)] + 7.567(0) - 8.784(0) = 19.93 \text{ kJ/mol}$
Nitrogen rich compound	2,5-Dimethyl-2H-tetrazole		$\Delta_{\text{fus}}H = 0.9781[0.6047(3) + 0.6211(6) + 2.750(4) + 1.424(0) + 3.048(0)] + 7.567(0) - 8.784(0) = 16.18 \text{ kJ/mol}$
	4,6-Dichloro-N-(2-chlorophenyl)-1,3,5-triazin-2-amine		$\Delta_{\text{fus}}H = 0.9781[0.6047(9) + 0.6211(5) + 2.750(4) + 1.424(0) + 3.048(3)] + 7.567(0.5) - 8.784(0.5) = 27.46 \text{ kJ/mol}$

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Figure captions

Fig. 1 Comparison of predicted fusion enthalpies by new method, Jain et al. method [30], and Mosaei Oskoei-Keshavarz [22] method

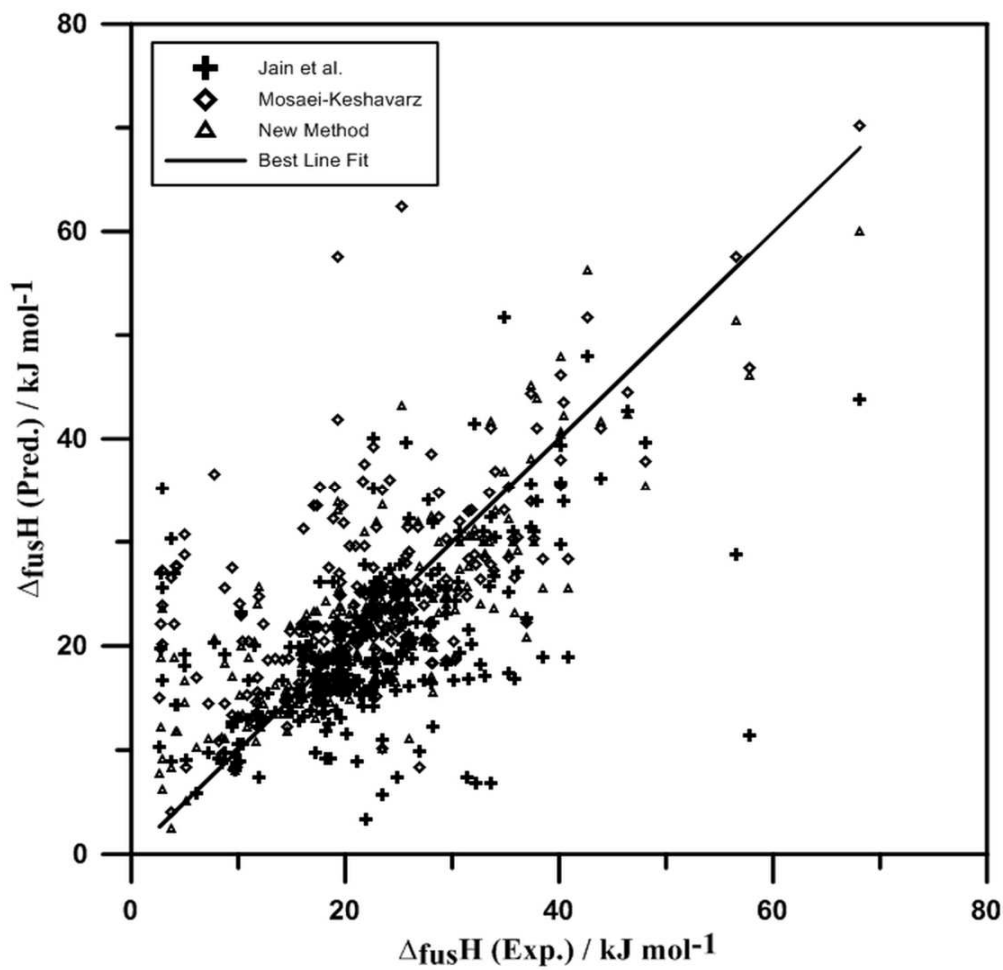


Table 1. Comparison of the calculated fusion enthalpies of energetic materials by Eq. (1), Eq. (2), Jain et al. [30], and Mosaei Oskoei-Keshavarz [22] methods with experimental data

No.	Name	$\Delta_{fus}H(exp)$ /kJ mol ⁻¹	$\Delta_{fus}H(predicted)/kJ\ mol^{-1}$							
			Ref. [30]	Dev.	Ref. [22]	Dev.	Eq. (1)	Dev.	Eq. (2)	Dev.
Acyclic nitramines:										
1.	N-Nitromethanimine (DIGEN)	23.45 [16]	11.02	12.43	10.11	13.34	10.19	13.26	9.97	13.48
2.	N-(aminomethyl)-N-nitronitramide	35.85 [47]	16.81	19.04	26.58	9.27	19.78	16.07	23.13	12.72
3.	2,4-Dinitro-2,4-diazapentane (DNAPTn)	16.36 [16]	20.06	-3.70	22.06	-5.70	23.48	-7.12	22.96	-6.60
4.	N,N'-Dimethyl-N,N'-dinitro-1,2-ethanediamine	29.40 [16]	23.06	6.34	30.25	-0.85	25.33	4.07	24.77	4.63
5.	2,4,6-Trinitro-2,4,6-triazaheptane (TNAHP)	34.01 [16]	30.41	3.60	36.84	-2.83	33.67	0.34	32.94	1.07
6.	2,4,7,9-Tetranitro-2,4,7,9-tetraazadecane	68.09 [16]	43.75	24.34	70.18	-2.09	45.71	22.38	59.85	8.24
7.	N-Methyl-N,2,4,6-tetranitroaniline (Tetryl)	25.86 [43]	24.88	0.98	31.48	-5.62	32.48	-6.62	31.77	-5.91
		26.78 [48]		1.90		-4.70		-5.70		-4.99
		22.90 [43]		-1.98		-8.58		-9.58		-8.87
8.	N-(4-Chlorophenyl)-N-methylnitramide	19.50 [47]	16.67	2.83	20.82	-1.32	16.93	2.57	16.56	2.94
9.	N-Methyl-N-(3-nitrophenyl)nitramide	25.30 [47]	19.08	6.22	25.36	-0.06	22.53	2.77	22.03	3.27
10.	2,4,6,8,10,12-Tetranitro-2,4,6,8,10,12-hexaazatridecane	109.1 [16]	61.45	47.62	106.6	2.49	64.26	44.81	93.12	15.95
11.	N-Ethyl-N-(2,4,6-trinitrophenyl)nitramide	23.51 [47]	21.11	2.40	35.00	-11.4	34.33	-10.82	33.57	-10.06
Dev. and ΔH_{fus} for the 11 acyclic nitramine compounds			26.21	9.39	37.75	-1.39	29.88	5.11	33.70	1.99
Cyclic nitramines:										
12.	1,3,3-Trinitroazetidine (TNAZ)	29.45 [14]	24.27	5.18	18.60	10.85	23.84	5.61	23.32	6.13
		30.31 [14]		6.04		11.71		6.47		6.99
13.	1,3-Dinitroimidazolidine (CPX)	25.10 [43]	23.69	1.41	23.75	1.35	22.24	2.86	21.75	3.35
		22.57 [16]		-1.12		-1.18		0.33		0.82
14.	1,3,5-Trinitroso-1,3,5-triazinane (TTT)	3.77 [43]	30.36	-26.59	26.59	-22.82	26.31	-22.54	8.17	-4.40
15.	1,3-Dinitro-5-nitroso-1,3,5-triazinane	25.97 [47]	32.24	-6.27	29.09	-3.12	29.16	-3.19	10.95	15.02
16.	1,3,5-Trinitro-1,3,5-triazinane (RDX)	37.66 [43]	31.04	6.62	30.34	7.32	30.58	7.08	29.91	7.75
		35.65 [16]		4.61		5.31		5.06		5.73
		32.90 [16]		1.86		2.56		2.32		2.99
		30.71 [16]		-0.33		0.37		0.13		0.80
17.	1,4-Dinitropiperazine (1,4-DNDC)	33.93 [16]	26.69	7.24	27.27	6.66	24.08	9.85	23.56	10.37
18.	1,3-Dinitro-1,3-diazacyclohexane	2.93 [43]	25.53	-22.60	27.27	-24.34	24.08	-21.15	23.56	-20.63
19.	1,5-Dinitro-3-nitroso-1,3,5-triazepane	2.90 [47]	35.19	-32.29	23.86	-20.96	31.01	-28.11	6.17	-3.27
20.	1,3,5-Trinitro-1,3,5-triazepane (TNACHP)	27.74 [16]	34.04	-6.30	25.11	2.63	32.43	-4.69	25.13	2.61
21.	1,3,5,7-Tetranitro-1,3,5,7-tetrazocane (HMX)	32.10 [16]	41.39	-9.29	28.78	3.32	40.78	-8.68	31.10	1.00
22.	1,7-Diazido-2,4,6-trinitro-2,4,6-triazaheptane	40.17 [47]	39.39	0.78	46.13	-5.96	48.93	-8.76	47.86	-7.69
23.	1,3-Dinitro-1,3-diazepane	2.80 [47]	26.97	-24.17	22.04	-19.24	25.93	-23.13	18.77	-15.97

No.	Name	$\Delta_{\text{fus}}H(\text{exp})$ /kJ mol ⁻¹	$\Delta_{\text{fus}}H(\text{predicted})/\text{kJ mol}^{-1}$							
			Ref. [30]	Dev.	Ref. [22]	Dev.	Eq. (1)	Dev.	Eq. (2)	Dev.
		3.98 [43]		-22.99		-18.06		-21.95		-14.79
24.	3,7-Dinitro-1,3,5,7-tetraaza-bicyclo[3.3.1]nonane	28.16 [49]	31.85	-3.69	20.29	7.87	31.43	-3.27	19.76	8.40
25.	1,3,5,7,9-Pentanitro-1,3,5,7,9-pentaazacyclodecane	34.93 [16]	51.73	-16.80	33.06	1.87	50.97	-16.04	36.68	-1.75
26.	4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane	36.10 [49]	27.04	9.06	30.38	5.72	29.75	6.35	29.09	7.01
27.	2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20)	42.70 [49]	47.90	-5.20	51.74	-9.04	57.44	-14.74	56.18	-13.48
28.	Trans-1,4,5,8-Tetranitro-1,4,5,8-tetraazadecaline	46.40 [16]	42.66	3.74	44.52	1.88	43.23	3.17	42.28	4.12
29.	1,1'-(3,7-Dinitro-1,3,5,7-tetrazocane-1, 5-diyl)bis(ethan-1-one) (DADN)	25.76 [50]	39.58	-13.82	28.63	-2.87	38.58	-12.82	25.43	0.33
Dev. and ΔH_{fus} for the 18 cyclic nitramine compounds			33.98	-6.04	29.86	-2.42	33.93	-5.83	26.65	0.06
Nitrate esters:										
30.	Methyl nitrate	8.24 [43]	9.21	-0.97	10.81	-2.57	9.49	-1.25	9.28	-1.04
31.	Ethyl nitrate	8.52 [43]	8.72	-0.20	9.66	-1.14	11.34	-2.82	11.09	-2.57
32.	Nitroglycerine (NG)	21.87 [47]	27.76	-5.89	21.81	0.06	25.98	-4.11	25.41	-3.54
		25.10 [48]		-2.66		3.29		-0.88		-0.31
33.	Isopropyl nitrate	10.01 [43]	10.50	-0.49	13.19	-3.18	13.18	-3.17	12.89	-2.88
34.	Diethyleneglycol dinitrate	25.40 [47]	26.23	-0.83	22.27	3.13	22.85	2.55	22.35	3.05
35.	Pentaerythritol Tetranitrate (PETN)	48.05 [51]	39.60	8.45	37.83	10.22	36.08	11.97	35.29	12.76
Dev. and ΔH_{fus} for the 6 nitrate ester compounds			20.34	-0.37	19.26	1.40	19.82	0.33	19.39	0.78
Polynitro arenes:										
36.	2-Chloro-1,3,5-trinitrobenzene	18.18 [51]	11.77	6.41	21.72	-3.54	24.71	-6.53	24.17	-5.99
37.	1-Chloro-2,4-dinitrobenzene	20.17 [47]	15.91	4.26	18.66	1.51	19.73	0.44	19.30	0.87
38.	2-Chloro-1,3-dinitrobenzene	18.95 [47]	15.91	3.04	18.66	0.29	19.73	-0.78	19.30	-0.35
39.	1,3,5-Trinitrobenzene (TNB)	14.81 [47]	19.84	-5.03	21.37	-6.56	22.28	-7.47	21.80	-6.99
		15.69 [13]		-4.15	21.37	-5.68		-6.59		-6.11
		16.74 [48]		-3.10	21.37	-4.63		-5.54		-5.06
40.	2,4,6-Trinitrophenol (Picric acid, PA)	17.10 [43]	21.81	-4.71	33.45	-16.35	23.71	-6.61	23.19	-6.09
		19.66 [48]		-2.15		-13.79		-4.05		-3.53
		17.41 [14]		-4.40		-16.04		-6.30		-5.78
41.	2,4,6-Trinitro-1,3-benzenediol (Styphnic acid)	33.50 [43]	25.70	7.80	34.70	-1.20	25.13	8.37	29.88	3.62
		28.80 [14]		3.10		-5.90		3.67		-1.08
42.	1,2-Dinitrobenzene	22.84 [43]	16.40	6.44	18.31	4.53	17.31	5.53	16.93	5.91
43.	1,3-Dinitrobenzene	19.68 [47]	15.24	4.44	18.31	1.37	17.31	2.37	16.93	2.75
		17.36 [43]		2.12		-0.95		0.05		0.43
44.	1,4-Dinitrobenzene	17.58 [47]	16.40	1.18	18.31	-0.73	17.31	0.27	16.93	0.65
		28.12 [43]		11.72		9.81		10.81		11.19
45.	2,3-Dinitrophenol	22.67 [47]	18.82	3.85	23.50	-0.83	18.73	3.94	23.62	-0.95
		26.24 [43]		7.42		2.74		7.51		2.62
46.	2,4-Dinitrophenol	26.19 [47]	18.82	7.37	23.50	2.69	18.73	7.46	23.62	2.57
		24.17 [43]		5.35		0.67		5.44		0.55

No.	Name	$\Delta_{fus}H(exp)$ /kJ mol ⁻¹	$\Delta_{fus}H(predicted)/kJ mol^{-1}$							
			Ref. [30]	Dev.	Ref. [22]	Dev.	Eq. (1)	Dev.	Eq. (2)	Dev.
47.	2,5-Dinitrophenol	23.73 [43]	18.82	4.91	23.50	0.23	18.73	5.00	23.62	0.11
48.	2,6-Dinitrophenol	22.91 [47]	17.52	5.39	19.56	3.35	18.73	4.18	18.32	4.59
		19.58 [43]		2.06		0.02		0.85		1.26
49.	3,4-Dinitrophenol	25.37 [47]	20.11	5.26	23.50	1.87	18.73	6.64	23.62	1.75
50.	1-Amino-2,4,6-trinitrobenzene (TNA)	28.15 [14]	22.30	5.85	24.90	3.25	25.66	2.49	24.49	3.66
51.	1,3-Diamino-2,4,6-trinitrobenzene (DATB)	35.25 [14]	25.12	10.13	35.33	-0.08	29.03	6.22	32.17	3.08
52.	(2,4-Dinitrophenyl)hydrazine	18.89 [47]	26.09	-7.20	32.27	-13.38	24.05	-5.16	22.92	-4.03
53.	2,4,6-Trinitrobenzene-1,3,5-triamine (TATB)	56.60 [14]	28.72	27.88	57.57	-0.97	32.40	24.20	51.36	5.24
54.	2,4,6-Trinitrobenzoic acid (TNBA)	31.60 [13]	21.53	10.07	28.35	3.25	25.74	5.86	30.47	1.13
55.	2,4-Dinitrobenzaldehyde	21.18 [47]	8.94	12.24	20.10	1.08	19.34	1.84	18.91	2.27
56.	2,4-Dinitrobenzoic acid	30.60 [47]	26.11	4.49	25.29	5.31	20.76	9.84	25.60	5.00
57.	3,4-Dinitrobenzoic acid	24.60 [47]	26.11	-1.51	25.29	-0.69	20.76	3.84	25.60	-1.00
58.	3,5-Dinitrobenzoic acid	22.80 [47]	26.11	-3.31	25.29	-2.49	20.76	2.04	25.60	-2.80
59.	2-Methyl-1,3,5-trinitrobenzene (TNT)	24.70 [43]	18.42	6.28	24.89	-0.19	24.13	0.57	23.60	1.10
		22.60 [48]		4.18		-2.29		-1.53		-1.00
		21.92 [51]		3.50		-2.97		-2.21		-1.68
		19.58 [14]		1.16		-5.31		-4.55		-4.02
		19.50 [13]		1.08		-5.39		-4.63		-4.10
60.	3-Methyl-2,4,6-trinitrophenol (TNCr)	26.74 [14]	22.30	4.44	26.14	0.60	25.55	1.19	25.00	1.74
61.	2-Methoxy-1,3,5-trinitrobenzene	19.64 [51]	21.03	-1.39	26.14	-6.50	25.55	-5.91	25.00	-5.36
62.	1-Methyl-2,4-dinitrobenzene	20.12 [43]	17.20	2.92	21.83	-1.71	19.15	0.97	18.74	1.38
		19.84 [51]	17.20	2.64	21.83	-1.99	19.15	0.69	18.74	1.10
63.	1-Methyl-2,3-dinitrobenzene	17.57 [47]	17.20	0.37	21.83	-4.26	19.15	-1.58	18.74	-1.17
64.	2-Methyl-1,3-dinitrobenzene	23.85 [47]	17.20	6.65	21.83	2.02		4.70		5.11
		19.28 [43]		2.08		-2.55		0.13		0.54
		17.10 [51]		-0.10		-4.73		-2.05		-1.64
		16.07 [43]		-1.13		-5.76		-3.08		-2.67
65.	4-Methyl-1,2-dinitrobenzene	18.83 [47]	17.20	1.63	21.83	-3.00	19.15	-0.32	18.74	0.09
66.	2-Methyl-3,5-dinitrophenol	19.41 [47]	19.61	-0.20	27.02	-7.61	20.58	-1.17	25.42	-6.01
67.	2,4-Dimethyl-1,3,5-trinitrobenzene (TNX)	38.49 [47]	18.90	19.59	28.41	10.08	25.98	12.51	25.41	13.08
		40.87 [13]		21.97		12.46		14.89		15.46
68.	3-Methyl-2,4,6-trinitro-N-(nitromethyl)aniline	19.33 [47]	18.41	0.92	41.90	-22.57	34.33	-15.00	32.97	-13.64
69.	2,4,6-Trimethyl-1,3,5-trinitrobenzene (TNMs)	30.72 [13]	19.39	11.33	31.93	-1.21	27.83	2.90	27.22	3.50
70.	1,4,5-Trinitronaphthalene (1,4,5-TNN)	27.49 [13]	20.09	7.40	20.68	6.81	25.95	1.54	25.38	2.11
71.	1,5-Dinitronaphthalene (1,5-DNN)	33.03 [13]	17.14	15.89	28.45	4.58	20.97	12.06	28.83	4.20
72.	1,8-Dinitronaphthalene (1,8-DNN)	35.23 [13]	17.40	17.83	28.45	6.78	20.97	14.26	28.83	6.40
73.	1-Nitronaphthalene	17.30 [47]	14.71	2.59	14.56	2.74	15.99	1.31	15.64	1.66
74.	2-(sec-Butyl)-4,6-dinitrophenol	21.81 [47]	15.70	6.11	37.59	-15.78	26.12	-4.31	30.84	-9.03
75.	Butyl 2,4,6-trinitrobenzoate	28.13 [47]	26.83	1.30	38.50	-10.37	33.12	-4.99	32.40	-4.27
76.	2,2',4,4',6,6'-Hexanitro-1,1'-biphenyl (HNB)	37.44 [13]	31.46	5.98	33.91	3.53	43.33	-5.89	37.99	-0.55

No.	Name	$\Delta_{\text{fus}}H(\text{exp})$ /kJ mol ⁻¹	$\Delta_{\text{fus}}H(\text{predicted})/\text{kJ mol}^{-1}$							
			Ref. [30]	Dev.	Ref. [22]	Dev.	Eq. (1)	Dev.	Eq. (2)	Dev.
77.	Bis(2,4,6-trinitrophenyl)sulfane (DIPS)	38.00 [13]	33.95	4.05	41.00	-3.00	44.75	-6.75	43.77	-5.77
78.	2,2'-Sulfonylbis(1,3,5-trinitrobenzene) (DIPSO)	40.39 [13]	33.96	6.43	43.51	-3.12	47.60	-7.21	42.16	-1.77
79.	Bis(2,4,6-trinitrophenyl)amine (Hexyl or DPA)	37.38 [13]	35.64	1.74	44.34	-6.96	46.70	-9.32	45.07	-7.69
80.	4,4'-Oxybis(nitrobenzene)	10.29 [47]	23.17	-12.88	22.93	-12.64	24.84	-14.55	19.91	-9.62
81.	2,3,5,7-Tetranitro-9H-xanthen-9-one	33.56 [47]	6.85	26.71	27.86	5.70	35.58	-2.02	30.41	3.15
82.	2,4,5,7-Tetranitro-9H-xanthen-9-one	32.20 [47]	6.85	25.35	27.86	4.34	35.58	-3.38	30.41	1.79
83.	2,4,7-Trinitro-9H-fluoren-9-one	23.50 [47]	5.64	17.86	23.55	-0.05	29.18	-5.68	24.15	-0.65
84.	1,2,7-Trinitro-9H-xanthen-9-one	11.89 [47]	7.31	4.58	24.81	-12.92	30.61	-18.72	25.54	-13.65
85.	2,3,7-Trinitro-9H-xanthen-9-one	24.91 [47]	7.31	17.60	24.81	0.10	30.61	-5.70	25.54	-0.63
86.	2,4,7-Trinitro-9H-xanthen-9-one	31.40 [47]	7.31	24.09	24.81	6.59	30.61	0.79	25.54	5.86
87.	2,2',4,4',6,6'-Hexanitrostilbene (HNS)	40.21 [13]	35.75	4.46	37.98	2.23	45.78	-5.57	40.38	-0.17
88.	3,3'-Dimethyl-2,2',4,4',6,6'-hexanitro-1,1'-biphenyl	33.69 [13]	32.43	1.26	40.96	-7.27	47.02	-13.33	41.60	-7.91
89.	1,2-Bis(2,4,6-trinitrophenyl)ethane (DPE)	43.85 [13]	36.19	7.66	40.96	2.89	47.02	-3.17	41.60	2.25
90.	Bis(3-methyl-2,4,6-trinitrophenyl)sulfane	57.78 [13]	11.44	46.34	46.80	10.98	47.02	10.76	45.99	11.79
Dev. and ΔH_{fus} for the 55 polynitro arene compounds			19.92	6.05	28.00	-1.62	27.08	0.09	27.27	-0.15
Polynitro heteroarenes:										
91.	2,4,6-Trinitropyridine	22.00 [47]	3.31	18.69	21.38	0.62	23.81	-1.81	23.29	-1.29
92.	4,6-Dinitrobenzofurazan 1-oxide	20.73 [47]	--	--	21.92	-1.19	24.41	-3.68	23.88	-3.15
93.	5-Nitro-8-hydroxyquinoline	19.61 [47]	13.07	6.54	19.76	-0.15	18.94	0.67	21.55	-1.94
94.	1-(2,4,6-Trinitrophenyl)-5,7-dinitro benzotriazole	40.10 [14]	29.81	10.29	35.50	4.60	45.98	-5.88	40.58	-0.48
Dev. and ΔH_{fus} for the 4 polynitro heteroarene compounds			15.40	11.84	24.64	0.97	28.29	-2.68	27.33	-1.72
Nitroaliphatics:										
95.	Nitromethane	9.70 [43]	8.10	1.60	9.56	0.14	8.07	1.63	7.89	1.81
96.	1,1,1-Trinitroethane	11.72 [47]	13.33	-1.61	14.53	-2.81	19.87	-8.15	10.65	1.07
97.	2,2,2-Trinitroethanol	2.72 [47]	19.73	-17.01	19.72	-17.00	21.29	-18.57	12.04	-9.32
98.	Nitroethane	9.85 [43]	8.72	1.13	8.41	1.44	9.91	-0.06	9.70	0.15
99.	2,2-Dinitropropane	2.64 [43]	10.23	-7.59	14.99	-12.35	16.74	-14.10	7.59	-4.95
100.	2,2-Dinitropropan-1-ol	2.85 [47]	16.63	-13.78	20.18	-17.33	18.16	-15.31	8.98	-6.13
101.	2,3-Dimethyl-2,3-dinitrobutane	8.80 [47]	19.14	-10.34	25.56	-16.76	22.28	-13.48	18.28	-9.48
102.	2,2-Dinitroadamantane	5.06 [47]	19.12	-14.06	30.71	-25.65	25.94	-20.88	16.59	-11.53
103.	1-Nitroadamantane	4.18 [47]	14.26	-10.08	27.65	-23.47	20.96	-16.78	11.72	-7.54
104.	2-Nitroadamantane	4.23 [47]	14.26	-10.03	27.65	-23.42	20.96	-16.73	11.72	-7.49
105.	2-Nitroadamantane-2-carbonitrile	4.98 [47]	18.02	-13.04	28.74	-23.76	23.69	-18.71	14.39	-9.41
Dev. and ΔH_{fus} for the 11 nitroaliphatic compounds			14.69	-8.62	20.70	-14.63	18.90	-12.83	11.78	-5.71
Nitroaromatics:										
106.	1,2,3,4,5-Pentafluoro-6-nitrobenzene	11.81 [52]	12.20	-0.39	17.00	-5.19	24.47	-12.66	23.93	-12.12
107.	1,2,4,5-Tetrachloro-3-nitrobenzene	19.46 [47]	17.09	2.37	16.65	2.81	22.04	-2.58	21.56	-2.10
108.	1,2-Dichloro-4-nitrobenzene	17.95 [47]	13.50	4.45	15.95	2.00	17.19	0.76	16.81	1.14
109.	1-Chloro-2-nitrobenzene	18.21 [47]	9.21	9.00	15.60	2.61	14.76	3.45	14.43	3.78
110.	1-Chloro-3-nitrobenzene	18.65 [47]	9.21	9.44	15.60	3.05	14.76	3.89	14.43	4.22

No.	Name	$\Delta_{\text{fus}}H(\text{exp})$ /kJ mol ⁻¹	$\Delta_{\text{fus}}H(\text{predicted})/\text{kJ mol}^{-1}$							
			Ref. [30]	Dev.	Ref. [22]	Dev.	Eq. (1)	Dev.	Eq. (2)	Dev.
111.	1-Chloro-4-nitrobenzene	18.03 [43]	13.62	4.41	15.60	2.43	14.76	3.27	14.43	3.60
		15.03 [47]		1.41		-0.57		0.27		0.60
		11.85 [43]		-1.77		-3.75		-2.91		-2.58
112.	2-Chloro-4-nitrophenol	20.88 [47]	16.18	4.70	20.79	0.09	16.18	4.70	21.12	-0.24
113.	4-Chloro-2-nitrophenol	22.69 [47]	16.18	6.51	20.79	1.90	16.18	6.51	21.12	1.57
114.	4-Chloro-3-nitrophenol	25.97 [47]	16.18	9.79	20.79	5.18	16.18	9.79	21.12	4.85
115.	2,6-Dichloro-4-nitroaniline	29.48 [47]	18.16	11.32	26.38	3.10	20.56	8.92	23.89	5.59
116.	2,6-Dichloro-3-nitroaniline	32.64 [52]	18.16	14.48	26.38	6.26	20.56	12.08	23.89	8.75
117.	Nitrobenzene	12.12 [43]	12.97	-0.85	15.25	-3.13	12.33	-0.21	12.06	0.06
		10.81 [43]	12.97	-2.16	15.25	-4.44	12.33	-1.52	12.06	-1.25
118.	2-Nitrophenol	17.05 [47]	15.38	1.67	20.44	-3.39	13.76	3.30	18.75	-1.70
119.	3-Nitrophenol	18.06 [47]	16.68	1.38	20.44	-2.38	13.76	4.31	18.75	-0.69
		21.30 [43]	16.68	4.62	20.44	0.86	13.76	7.55	18.75	2.55
120.	4-Nitrophenol	11.00 [47]	16.68	-5.68	20.44	-9.44	13.76	-2.76	18.75	-7.75
		19.30 [43]		2.62		-1.14		5.55		0.55
		24.27 [43]		7.59		3.83		10.52		5.52
		30.12 [43]		13.44		9.68		16.37		11.37
		16.11 [43]		0.92		18.78		-2.67		15.70
122.	3-Nitroaniline	23.68 [43]	16.48	7.20	25.68	-2.00	15.70	7.98	19.14	4.54
123.	4-Nitroaniline	21.09 [43]	16.48	4.61	25.68	-4.59	15.70	5.39	19.14	1.95
124.	2-Nitrobenzonitrile	15.72 [47]	15.79	-0.07	16.35	-0.63	15.07	0.65	14.74	0.98
125.	3-Nitrobenzonitrile	20.49 [47]	15.79	4.70	16.35	4.14	15.07	5.42	14.74	5.75
126.	4-Nitrobenzonitrile	17.73 [47]	15.79	1.94	16.35	1.38	15.07	2.66	14.74	2.99
127.	2-Nitrobenzoic acid	27.99 [43]	22.03	5.96	22.24	5.75	15.78	12.21	20.73	7.26
128.	3-Nitrobenzoic acid	19.33 [43]	22.27	-2.94	22.24	-2.91	15.78	3.55	20.73	-1.40
		21.40 [43]		-0.87		-0.84		5.62		0.67
129.	4-Nitrobenzoic acid	36.90 [43]	22.67	14.23	22.24	14.66	15.78	21.12	20.73	16.17
130.	5-Nitro-1,3-benzodioxole	28.20 [47]	12.24	15.96	18.30	9.90	15.78	12.42	15.44	12.76
131.	1-Methyl-4-nitrobenzene	16.81 [43]	13.76	3.05	18.77	-1.96	14.18	2.63	13.87	2.94
132.	1-Methyl-3-nitrobenzene	19.20 [52]	13.76	5.44	18.77	0.43	14.18	5.02	13.87	5.33
133.	3-Methyl-4-nitrophenol	27.40 [47]	16.68	10.72	23.96	3.44	15.60	11.80	20.56	6.84
134.	5-Methyl-2-nitrophenol	20.79 [47]	16.68	4.11	23.96	-3.17	15.60	5.19	20.56	0.23
135.	2-Methoxy-4-nitrophenol	21.69 [47]	15.33	6.36	25.22	-3.53	17.03	4.66	21.95	-0.26
136.	2-Methoxy-5-nitrophenol	21.43 [47]	15.33	6.10	25.22	-3.79	17.03	4.40	21.95	-0.52
137.	4-Methoxy-2-nitrophenol	22.42 [47]	15.33	7.09	25.22	-2.80	17.03	5.39	21.95	0.47
138.	4-Nitroisobenzofuran-1,3-dione	18.40 [52]	18.95	-0.55	17.11	1.29	16.57	1.83	16.21	2.19
139.	5-Nitroisobenzofuran-1,3-dione	17.14 [52]	18.95	-1.81	17.11	0.03	16.57	0.57	16.21	0.93
140.	2,3-Dihydro-6-nitro-1,4-benzodioxin	24.27 [47]	25.22	-0.95	21.82	2.45	17.63	6.64	17.24	7.03
141.	2-Nitronaphthalene	14.50 [47]	14.71	-0.21	14.56	-0.06	15.99	-1.49	15.64	-1.14
142.	N-Phenyl 4-nitrobenzaldehyde imine	24.56 [47]	23.22	1.34	22.70	1.86	22.42	2.14	17.54	7.02

No.	Name	$\Delta_{\text{fus}}H(\text{exp})$ /kJ mol ⁻¹	$\Delta_{\text{fus}}H(\text{predicted})/\text{kJ mol}^{-1}$							
			Ref. [30]	Dev.	Ref. [22]	Dev.	Eq. (1)	Dev.	Eq. (2)	Dev.
143.	9-Nitroanthracene	20.10 [47]	11.52	8.58	19.71	0.39	19.65	0.45	19.22	0.88
144.	2,4,6-Tri-tert-butylnitrobenzene	19.25 [47]	15.92	3.33	57.51	-38.26	34.49	-15.24	33.74	-14.49
Dev. and $\Delta_{\text{fus}}H$ for the 39 nitroaromatic compounds			16.13	4.31	20.97	-0.24	16.75	4.04	18.58	2.03
Cyclic and (Acyclic) [#] peroxides:										
145.	3,3,6,6-Tetramethyl-1,2,4,5-tetraoxane (DADP)	24.70 [53]	15.70	9.00	26.14	-1.44	16.78	7.92	16.41	8.29
146.	3,3,6,6,9,9-Hexamethyl-1,2,4,5,7,8-hexaoxonane	22.60 [53]	40.05	-17.45	39.21	-16.61	25.16	-2.56	24.61	-2.01
147.	Benzoyl peroxide [#]	22.59 [47]	35.20	-12.61	27.50	-4.91	20.37	2.22	19.93	2.66
Dev. and $\Delta_{\text{fus}}H$ for the 3 cyclic and acyclic peroxides			30.32	-7.02	30.95	-7.65	20.77	2.53	20.32	2.98
Nitrogen rich and nitrogen compounds:										
148.	Cyanamide	8.76 [47]	9.80	-1.04	14.50	-5.74	7.35	1.41	10.97	-2.21
		7.27 [43]		-2.53		-7.23		-0.08		-3.70
149.	1H-Tetrazole	17.70 [47]	18.41	-0.71	18.59	-0.89	12.85	4.85	16.35	1.35
		18.40 [43]		-0.01		-0.19		5.55		2.05
150.	Nitroguanidine (NQ)	11.49 [14]	20.07	-8.58	12.51	-1.02	16.94	-5.45	20.35	-8.86
151.	Monomethylhydrazine	10.42 [43]	10.61	-0.19	20.46	-10.04	9.83	0.59	13.40	-2.98
152.	Guanidine nitrate	24.79 [51]	--	--	21.41	3.38	19.60	5.19	22.96	1.83
153.	1H-1,2,4-Triazole	16.10 [43]	17.52	-1.42	18.58	-2.48	11.32	4.78	14.86	1.24
154.	5-Nitro-3H-1,2,4-triazol-3-one (NTO)	27.00 [54]	9.94	17.06	8.35	18.65	16.48	10.52	27.47	-0.47
155.	Cyanoguanidine	22.96 [47]	22.73	0.23	15.22	7.74	14.69	8.27	18.16	4.80
156.	1-Methyl-1H-tetrazole	15.70 [47]	12.86	2.84	15.22	0.48	14.69	1.01	14.37	1.33
157.	2-Methyl-2H-tetrazole	12.37 [47]	12.86	-0.49	22.11	-9.74	14.69	-2.32	14.37	-2.00
158.	5-Methyl-1H-tetrazole	16.00 [47]	19.21	-3.21	22.11	-6.11	14.69	1.31	18.16	-2.16
159.	1H-1,2,4-Triazol-3-amine	21.93 [47]	21.04	0.89	22.11	-0.18	14.69	7.24	18.16	3.77
160.	1,3-Dinitro-1,3-diazacyclobutane	26.32 [16]	20.69	5.63	20.23	6.09	20.39	5.93	19.94	6.38
161.	N,N-Dimethylnitramide (DMNA)	17.26 [16]	9.71	7.55	16.62	0.64	13.28	3.98	12.99	4.27
162.	N,N'-Dinitroethylenediamine (EDNA)	29.50 [47]	25.75	3.75	25.43	4.07	21.63	7.87	24.94	4.56
		23.20 [16]		-2.55		-2.23		1.57		-1.74
163.	1,1-Dimethylhydrazine (UDMH)	10.07 [43]	8.91	1.16	23.99	-13.92	11.68	-1.61	15.21	-5.14
164.	Ethane-1,2-diamine	22.58 [43]	14.18	8.40	23.99	-1.41	11.68	10.90	15.21	7.37
165.	1,3,5-Triazine	14.56 [43]	15.18	-0.62	12.23	2.33	11.93	2.63	11.67	2.89
166.	1H-Imidazole	12.80 [43]	15.44	-2.64	18.57	-5.77	9.80	3.00	13.37	-0.57
167.	1H-Pyrazole	14.20 [47]	16.72	-2.52	18.57	-4.37	9.80	4.40	13.37	0.83
168.	1,5-Dimethyl-1H-tetrazole	14.70 [47]	13.65	1.05	18.74	-4.04	16.54	-1.84	16.18	-1.48
169.	2,5-Dimethyl-2H-tetrazole	13.50 [47]	13.65	-0.15	18.74	-5.24	16.54	-3.04	16.18	-2.68
170.	1,1,2-Trimethylhydrazine	9.48 [43]	12.61	-3.13	27.51	-18.03	13.53	-4.05	17.01	-7.53
171.	N,N'-Dimethyl-N,N'-dinitroethanediamide	23.40 [16]	26.50	-3.10	22.13	1.27	25.69	-2.29	25.13	-1.73
172.	N-Acetyl-3,3-dinitroazetidine	25.65 [47]	24.07	1.58	20.86	4.79	22.74	2.91	22.24	3.41
173.	Benzohydrazide	25.70 [47]	23.33	2.37	27.95	-2.25	16.13	9.57	19.56	6.14
174.	4,6-Dichloro-N-(2-chlorophenyl)-1,3,5-triazin-2-amine	31.48 [52]	16.79	14.69	32.91	-1.43	28.69	2.79	27.46	4.02
175.	Trans-Azobenzene	22.53 [47]	15.81	6.72	25.49	-2.96	18.97	3.56	18.55	3.98

No.	Name	$\Delta_{fus}H(exp)$ /kJ mol ⁻¹	$\Delta_{fus}H(predicted)/kJ mol^{-1}$							
			Ref. [30]	Dev.	Ref. [22]	Dev.	Eq. (1)	Dev.	Eq. (2)	Dev.
176.	4-Amino-4'-nitroazobenzene	31.88 [47]	20.12	11.76	33.14	-1.26	27.32	4.56	30.50	1.38
177.	4-Aminoazobenzene	21.70 [47]	14.23	7.47	35.92	-14.22	22.34	-0.64	21.24	0.46
178.	1,2-Diphenylhydrazine	17.65 [47]	26.09	-8.44	35.37	-17.72	20.21	-2.56	19.16	-1.51
179.	Methanamine ⁺	6.13 [43]	5.91	0.22	16.93	-10.80	6.46	-0.33	10.10	-3.97
180.	Propane-1,2-diamine ⁺	18.42 [43]	12.52	5.90	27.51	-9.09	13.53	4.89	17.01	1.41
181.	2-Aminobenzoic acid ⁺	20.38 [43]	18.24	2.14	29.60	-9.22	14.18	6.20	22.95	-2.57
182.	3-Aminobenzoic acid ⁺	21.84 [43]	22.75	-0.91	29.60	-7.76	14.18	7.66	22.95	-1.11
183.	4-Aminobenzoic acid ⁺	20.92 [43]	22.75	-1.83	29.60	-8.68	14.18	6.74	22.95	-2.03
184.	Naphthalene-1,8-diamine ⁺	16.15 [47]	13.22	2.93	31.30	-15.15	17.76	-1.61	21.15	-5.00
185.	Diphenylamine ⁺	19.90 [47]	21.06	-1.16	31.83	-11.93	16.84	3.06	15.86	4.04
186.	Benzidine ⁺	19.10 [47]	21.75	-2.65	35.37	-16.27	20.21	-1.11	19.16	-0.06
187.	4,4'-Oxydianiline ⁺	7.74 [47]	20.23	-12.49	36.62	-28.88	21.63	-13.89	20.55	-12.81
188.	4,4'-Oxybis(benzene-1,2-diamine) ⁺	25.30 [47]	19.45	5.85	62.40	-37.10	28.38	-3.08	43.04	-17.74
189.	1-Aminoanthracene-9,10-dione ⁺	28.78 [47]	27.40	1.38	32.44	-3.66	19.65	9.13	23.01	5.77
190.	1,4-Diaminoanthracene-9,10-dione ⁺	24.20 [47]	27.4	-3.20	35.97	-11.77	23.02	1.18	27.06	-2.86
Dev. and ΔH_{fus} for the 43 nitrogen rich and (amine)⁺ compounds			17.65	1.07	24.85	-5.64	16.67	2.38	19.43	-0.43
The other compounds:										
191.	Acetylene	3.76 [47]	8.89	-5.13	4.06	-0.30	2.45	1.31	2.40	1.36
192.	Ethylene oxide (Oxirane)	5.17 [43]	8.98	-3.81	8.30	-3.13	5.12	0.05	5.01	0.16
193.	Phenylacetylene	9.46 [47]	12.17	-2.71	13.28	-3.82	8.56	0.90	8.38	1.08
194.	Diphenylacetylene	21.50 [47]	15.46	6.04	22.49	-0.99	14.68	6.82	14.36	7.14
Dev. and ΔH_{fus} for the 4 other compounds			11.38	-1.40	12.03	-2.06	7.70	2.27	7.54	2.44
Average values of all of the 194 energetic compounds			19.97	2.54	25.63	-2.77	22.36	0.43	22.49	0.20

(Compound) [#] = Acyclic peroxides.(Compound) ⁺ = amine compounds.

Table 2.

Correcting functions account for the presence of different molecular fragments

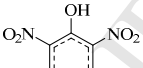
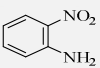
Molecular moieties	Effect on predicted $\Delta_{fus} H$		Comment
	$(\Delta_{fus} H)^{Inc}_{Non-add}$	$(\Delta_{fus} H)^{Dec}_{Non-add}$	
-OH and -COOH groups	0.7		In aromatic compounds
	0.0		In  Fragments
-NH ₂ group	0.5		For one or two -NH ₂ groups
	2.6		For more than two -NH ₂ groups
	0.0		In  Fragments
>NH group	0.5		-
>NNO ₂ group	$n_{NNO_2} - 2$		In acyclic nitramines
-N(C=O)N- fragment	1.5		-
Ar-X-Ar nitroaromatics		0.5	-
		0.0	when X is S
Cyclic nitramines		$\frac{m_{cyc} - 6}{4} + 0.5$	Rings with more than 6 members
-NO ₂ group		1.0	Nitroalkanes
-N=N=O group		2.0	-

Table 3. Comparison of the average deviations of Eq. (1), Eq. (2), Jain et al. [30] and Mosaei Oskoei-Keshavarz [22] methods

Class	Classification of energetic materials	Number of energetic materials	Ref. [30]	Ref. [22]	Eq. (1)	Eq. (2)
			Dev.	Dev.	Dev.	Dev.
I	Acyclic nitramines	11	9.39	-1.39	5.11	1.99
II	Cyclic nitramines	18	-6.04	-2.42	-5.83	0.06
III	Nitrate esters	6	-0.37	1.40	0.33	0.78
IV	Polynitro arenes	55	6.05	-1.62	0.09	-0.15

V	Polynitro heteroarenes	4	11.84	0.97	-2.68	-1.72
VI	Nitroaliphatics	11	-8.62	-14.63	-12.83	-5.71
VII	Nitroaromatics	39	4.31	-0.24	4.04	2.03
VIII	Cyclic and (acyclic) peroxides	3	-7.02	-7.65	2.53	2.98
IX	Nitrogen rich and (amine) compounds	43	1.07	-5.64	2.38	-0.43
X	The other compounds	4	-1.40	-2.06	2.27	2.44
(I-X)	All of the energetic materials	194	2.54	-2.77	0.43	0.20

Table 4. Statistical parameters of Eqs. (1) and (2) as well as Jain et al. [30] and Mosaei Oskoei-Keshavarz [22] methods

Parameter	Ref. [30]	Ref. [22]	Eq. (1)	Eq. (2)
Mean error (ME)	2.54	-2.77	0.43	0.20
Root mean square error (RMS)	9.88	8.92	8.72	6.03
Mean absolute error (MAE)	6.70	6.04	6.29	4.45
Maximum of errors (Highest deviations)	47.62	38.26	44.81	20.63

- An improved reliable method is introduced for prediction of enthalpy of fusion of organic energetic compounds.
- It requires only molecular structure of the compound.
- It gives good results as compared to two of the best available methods for 194 different energetic compounds.

ACCEPTED MANUSCRIPT