

Prediction of heats of sublimation of energetic compounds using their molecular structures

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Abstract A simple approach is presented to predict the heats of sublimation 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 molecular masses and two correcting functions that depend on intra- and intermolecular interactions. In contrast to other predictive methods, such as quantum mechanical calculations, the present approach can be easily applied for energetic compounds containing complex molecular structure, without using computer codes. The predicted results of the model have been compared with experimental data of 213 different energetic compounds.

Keywords Sublimation enthalpy · Energetic materials · Molecular mass · Correlation · Structural parameter

List of symbols

$\Delta_{\text{sub}}H$	Heat of sublimation (kJ mol^{-1})
F_{attract}	Correcting function due to intermolecular attractions
F_{repul}	Correcting function due to intermolecular repulsions

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M_{rev} Revised molecular mass (g mol^{-1})

Introduction

For synthesis and development of a new energetic compound, significant resources must be expended to determine its thermodynamic and physical properties as well as sensitivity to external stimuli. Reliable predictive methods allow experimental researchers and chemical industries to spend resources on those energetic molecules that have desired performance, sensitivity, thermochemical and physical properties. For example, some reliable simple methods have been recently introduced to predict solid to liquid phase changes of energetic compounds, i.e., melting point [1–6], enthalpy [7–10] and entropy of fusion [11, 12].

Organic explosives can coarsen during their storage because there is a combination of kinetic processes such as sublimation, recrystallization, and diffusion. This situation may reduce the surface area of the organic explosives, which influence the physical properties of the stored explosives. Especially, reducing the surface area of energetic compounds will cause to decrease their initiation sensitivity. Thus, sublimation properties are important factors for understanding the coarsening mechanism [13, 14]. The knowledge of heat of sublimation and vapor pressure can also provide the platform to increase the robustness of the detection techniques and to design new technology for detecting explosive particles from concealed devices [15]. Moreover, sublimation properties of explosives are associated with the environmental aspect because sublimation of organic explosives causes a long-term effect on soil, water, and air. The secondary explosives are the most important class of energetic materials, which can sublimate

in the room temperature. Thus, understanding the sublimation properties of the pure organic explosives are required to study their toxic effects in the environment during their storage [16].

The heat of sublimation can be regarded as one of the best parameters for the characterization of the intermolecular interactions within a crystal. One might estimate heat of fusion and heat of vaporization separately in order to obtain heat of sublimation, even though liquid cannot exist at the pressure and temperature in question. It is difficult to use the Clausius–Clapeyron equation for calculation of the heat of sublimation from solid vapor pressure data because the known sublimation pressures at the melting point are rare [17]. Due to importance of solid phase heat of formation of an energetic compound in prediction of its performance through various computer codes such as CHEETAH [18], ISPBKW [19], LOTUSES [20], and EDPHT [21], it can also be calculated by combining the predicted heat of sublimation and gas phase heat of formation according to Hess's law [22].

Since experimental data of the heats of sublimation of energetic compounds are rare, it is important to develop predictive methods. Bondi [23] proposed a group additivity scheme for prediction of the enthalpies of sublimation, which is fairly accurate for hydrocarbons and low-polarity molecules. But for those compounds containing strong electrostatic interactions in the crystal, for example, CHNO compounds, substantial errors occur in prediction of the enthalpies of sublimation [24]. Several quantum mechanical calculations and molecular simulations have been introduced for prediction of heats of sublimation in some classes of small organic energetic compounds [25–30]. For example, Hu et al. [28] have used the first-principles density-functional calculations of the electronic properties of the molecular surfaces to predict the heats of sublimation of energetic materials. Quantum mechanical methods require high-speed computers, special programs, and proficient users; moreover, it is difficult to use them for large molecules. A new complex method on the basis of neural network has been recently introduced by using the number of occurrences of 172 chemical groups on the chemical structures of pure compounds to predict the enthalpy of sublimation [31]. Several different approaches have also been introduced for calculation of the heat of sublimation in some classes of energetic compounds. Zeman and Krupka [32] introduced some relationships between lattice energies and heats of sublimation of some polynitro compounds. For nitroaromatics, it was indicated that elemental composition and the contribution of some specific groups attached to aromatic ring can be used to predict their heats of sublimation [33]. It was also shown that the heats of sublimation of nitramines can be predicted on the basis of their molecular masses and one structural parameter [34].

Since these methods cannot be used for nitroaliphatics and nitrate esters, a simple model has been recently developed to predict heats of sublimation of these classes of energetic compounds [35]. The purpose of this work is to introduce a simple approach for prediction of heats of sublimation 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. The present model is based on molecular masses and two correcting functions that depend on intermolecular attractions and repulsion. It will be shown that the new correlation can also be applied to halogenated energetic materials as well as energetic materials containing complex molecular structures. For several CHNO energetic compounds, the predicted results will be compared with the computed results of complex quantum mechanical methods [26, 27].

Development of the new model

The study of the heats of sublimation 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, has shown that it is possible to extend our previous works [33–35] through introducing a general simple correlation with higher accuracy and better precision. Previous studies [33–35] have shown that molecular mass is an important parameter for prediction of the heat of sublimation of some classes of energetic compounds. For nitroaromatics containing halogens attached to aromatic ring and hydrogen-free nitro compounds, it was found that the molecular mass should be revised because their effects may be different and the role of their atomic masses is negligible. However, it is necessary to ignore the contributions of halogens in calculating molecular mass of the mentioned compounds. Meanwhile, for the other classes of halogenated energetic compounds, the contribution of halogens should be considered in calculating the molecular mass. Thus, the revised molecular mass (M_{rev}) can be defined as the molecular mass of energetic compound except halogenated nitroaromatics and hydrogen-free nitro compounds.

Beside molecular mass, intra- and intermolecular interactions are also important factors for estimating the heats of sublimation. Various studies of different structural parameters have shown that the heat of sublimation ($\Delta_{\text{sub}}H$) should be adjusted by inclusion of two correcting functions related to intermolecular attractions (F_{attract}) and repulsions (F_{repul}). For example, in the presence of some polar groups, such as $-\text{COOH}$, $-\text{OH}$ and $-\text{NH}_2$, the intermolecular attractions are high so that it is necessary to include an

increasing correcting function, while the reverse situation can be observed for the existence of some structural parameters, such as the attachment of bulky alkyl groups to the aromatic rings, which need to include a decreasing correcting function.

Experimental data of 213 energetic compounds have been collected from different sources to develop the new correlation. The latest reported experimental values of the NIST Chemistry Web Book [36] as well as the new reported values in the literature, especially Ref. [37], were chosen for constructing the model. The data set was divided into two sets, i.e., training set includes 125 molecules (60 % of data points) and validation set includes 88 molecules (40 % of data points). Training and validation data sets were given in Tables 1 and 2, respectively. Tables S.1 and S.2, which are available in supporting information, contain the name of energetic molecules, their molecular structures, and experimental values of sublimation enthalpies of energetic compounds used in training and validation sets, respectively.

Multiple linear regression method [38] and training data set were used to find the relative contribution of M_{rev} , F_{attract} , and F_{repul} for prediction of $\Delta_{\text{sub}}H$. For multiple linear regression method, the left-division technique for solving linear equations uses the least squares method because the equation set is overdetermined [38]. Thus, the optimized correlation can be given as follows:

$$\Delta_{\text{sub}}H = 52.89 + 0.2689M_{\text{rev}} + 15.13F_{\text{attract}} - 13.29F_{\text{repul}} \quad (1)$$

where $\Delta_{\text{sub}}H$ is in kJ mol^{-1} . As indicated in Eq. (1), the coefficients of F_{attract} and F_{repul} have positive and negative signs, respectively, which are consistent with the role of increasing and decreasing of these correcting functions.

The predictive ability of model, Eq. (1), was evaluated by examining it for validation set, given in Table 2. Since quantum mechanical computations of Rice and coworkers [26] as well as Byrd et al. [27] were available for several energetic compounds, a comparison of the present method with quantum mechanical methods is also given in Table 2 for 24 energetic compounds as external validation data set.

Results and discussion

The role of specific functional groups and molecular moieties in F_{attract} and F_{repul}

The values of F_{attract} and F_{repul} , which were reported in Table 3, can be specified according to the following conditions for the presence of various functional groups and molecular moieties:

- Presence of* $-\text{COOH}$, $-\text{OH}$, $\text{N}^+\text{O}^-\text{N}^+\text{O}^-$, $-\text{NH}_2$ (or $-\text{NH}-$), and $\text{NH}=\text{C}(\text{NH})_2$ polar groups: For the existence of these polar groups, the contribution of F_{attract} is considerable because there are intermolecular hydrogen bonding and dipole intermolecular attractions. The values of F_{attract} can be specified as: (a) $F_{\text{attract}} = 2.0$ for the compounds containing at least one $-\text{C}(=\text{O})\text{OH}$ or two $-\text{OH}$ functional groups. However, for nitroaromatics containing two $-\text{OH}$ groups, nitro groups should be separated from $-\text{OH}$ at least by one $=\text{CH}-$ group, e.g., 4-nitrobenzene-1,2-diol, because intramolecular hydrogen bonding of a group can reduce its ability to form intermolecular hydrogen bonds. The presence of nitro group in ortho position with respect to $-\text{OH}$ reduces its attracting effect so that $F_{\text{attract}} = 0.0$ in these compounds, e.g., 2,4,6-Trinitro-1,3-benzenediol (styphnic acid). (b) It was indicated that the presence of amino group under certain conditions can reduce the sensitivity of energetic compounds with respect to different kinds of stimuli such as impact [39, 40], electric spark [41, 42] and shock [43]. Also, the thermal stability of explosives can be increased by entering the amino groups into nitroaromatic structures [43]. In other word, amino groups can increase the heat of sublimation. The value of F_{attract} equals the number of $-\text{NH}_2$, $-\text{NH}-$, or $\text{N}^+\text{O}^-\text{N}^+\text{O}^-$ groups. (c) It was indicated that $\text{NH}=\text{C}(\text{NH})_2$ molecular fragments can improve the thermodynamic stability and insensitivity of corresponding nitramines [40, 44–46]. For nitramines or polynitrogen organic compounds with this molecular fragment, there is a large intermolecular attraction so that the value of F_{attract} is 4.7.
- Nitramines:* (a) The direct electrostatic interactions are dominant in crystals of polynitramines which have $\text{NO}_2-\text{N}(\text{H})-\text{N}(\text{H})-\text{NO}_2$ molecular fragment; thus, their heats of sublimation tend to increase [34, 35]. For these compounds, F_{attract} is 1.0 and 2.0 in acyclic and cyclic nitramines, respectively. This situation confirms that intermolecular electrostatic attractions of nitramines are enhanced in cyclic structures. (b) For the other acyclic nitramines, F_{repul} is 2.6.
- Nitroaliphatic compounds:* For this category of energetic compounds, the presence of nitro groups can reduce intermolecular forces. Thus, the value of F_{repul} is equal to 2.6 in these compounds.
- Alkylated nitroaromatics:* Increasing the size of alkyl substituents in aromatic rings can lead to decrease the

Table 1 Comparison of predicted heats of sublimation/ kJ mol^{-1} of the new method with the experimental data, in training set

Name	Formula	$\Delta_{\text{sub}}H(\text{exp})/\text{kJ mol}^{-1}$	$\Delta_{\text{sub}}H(\text{cal})/\text{kJ mol}^{-1}$	Dev.
Iodotrinitromethane	CIN_3O_6	49.0 [36]	58.7	-9.7
Cyanamide	CH_2N_2	75.2 [37]	79.3	-4.1
1H-Tetrazole	CH_2N_4	88.2 [37]	86.9	1.3
1H-Tetrazol-5-amine	CH_3N_5	112.6 [37]	106.0	6.6
Hydrazinecarbothiohydrazide	$\text{CH}_6\text{N}_4\text{S}$	152.1 [37]	152.6	-0.5
1,2-Dichloro-1,1,2,2-tetranitroethane	$\text{C}_2\text{Cl}_2\text{N}_4\text{O}_8$	88.3 [36]	74.3	14.0
1-Fluoro-1,1,2,2,2-pentanitroethane	$\text{C}_2\text{FN}_5\text{O}_{10}$	69.0 [36]	86.7	-17.7
2-Fluoro-2,2-dinitroethanol	$\text{C}_2\text{H}_3\text{FN}_2\text{O}_5$	55.6 [37]	59.8	-4.2
1,1,1-Trinitroethane	$\text{C}_2\text{H}_3\text{N}_3\text{O}_6$	72.0 [37]	62.7	9.3
1,3-Dinitro-1,3-diazacyclobutane	$\text{C}_2\text{H}_4\text{N}_4\text{O}_4$	94.2 [50]	92.7	1.5
1,1-Diamino-2,2-dinitroethene (FOX-7)	$\text{C}_2\text{H}_4\text{N}_4\text{O}_4$	108.7 [28]	116.3	-7.6
2-Methyl-1H-tetrazol-5-amine	$\text{C}_2\text{H}_5\text{N}_5$	90.6 [37]	94.7	-4.1
1,3-Dichloro-1,1,3,3-tetranitropropane	$\text{C}_3\text{H}_2\text{Cl}_2\text{N}_4\text{O}_8$	93.7 [36]	97.1	-3.4
2-Methyl-4-nitro-1,2,3-triazole	$\text{C}_3\text{H}_4\text{N}_4\text{O}_2$	74.7 [37]	87.3	-12.6
2,4-Dinitro-2,4-diazapentane	$\text{C}_3\text{H}_8\text{N}_4\text{O}_4$	108.8 [24]	112.2	-3.4
Fumaronitrile	$\text{C}_4\text{H}_2\text{N}_2$	68.6 [37]	73.9	-5.3
2-Nitrofuran	$\text{C}_4\text{H}_3\text{NO}_3$	75.3 [37]	83.3	-8.0
<i>N,N</i> -Bis (2,2,2-trinitroethyl) nitramide	$\text{C}_4\text{H}_4\text{N}_8\text{O}_{14}$	117.6 [37]	122.7	-5.1
1-Fluoro-1,1,3,3-tetranitrobutane	$\text{C}_4\text{H}_5\text{FN}_4\text{O}_8$	91.6 [36]	87.2	4.4
1-Iodo-1,1,3,3-tetranitrobutane	$\text{C}_4\text{H}_5\text{IN}_4\text{O}_8$	99.2 [36]	116.2	-17.0
1,1,3,3-Tetranitrobutane	$\text{C}_4\text{H}_6\text{N}_4\text{O}_8$	87.9 [37]	82.4	5.5
2,2,3,3-Tetranitrobutane	$\text{C}_4\text{H}_6\text{N}_4\text{O}_8$	78.2 [37]	82.4	-4.2
2-Methyl-1,1,1,3-tetranitropropane	$\text{C}_4\text{H}_6\text{N}_4\text{O}_8$	91.2 [37]	82.4	8.8
1,3,5,7-Tetranitro-1,3,5,7-tetrazocane (HMX)	$\text{C}_4\text{H}_8\text{N}_8\text{O}_8$	161.0 [51]	162.8	-1.8
2,4,6-Trinitropyridine	$\text{C}_5\text{H}_2\text{N}_4\text{O}_6$	101.7 [37]	110.5	-8.8
2,4,6-Trinitropyridine 1-oxide	$\text{C}_5\text{H}_2\text{N}_4\text{O}_7$	106.3 [37]	114.8	-8.5
5-Nitrofuran-2-carbaldehyde	$\text{C}_5\text{H}_3\text{NO}_4$	75.3 [36]	90.8	-15.5
Benzotrifuroxan	$\text{C}_6\text{N}_6\text{O}_6$	172.5 [37]	166.1	6.4
2-Chloro-1,3,5-trinitrobenzene	$\text{C}_6\text{H}_2\text{ClN}_3\text{O}_6$	103.8 [37]	109.9	-6.1
1,2-Dichloro-4-nitrobenzene	$\text{C}_6\text{H}_3\text{Cl}_2\text{NO}_2$	85.8 [37]	85.5	-2.3
1,3-Dichloro-5-nitrobenzene	$\text{C}_6\text{H}_3\text{Cl}_2\text{NO}_2$	83.2 [37]	85.5	0.3
1,4-Dichloro-2-nitrobenzene	$\text{C}_6\text{H}_3\text{Cl}_2\text{NO}_2$	87.4 [37]	85.5	1.9
1,4-Dibromo-2-nitrobenzene	$\text{C}_6\text{H}_3\text{Br}_2\text{NO}_2$	97.0 [37]	85.5	11.5
4-Nitrobenzofurazan-1-oxide	$\text{C}_6\text{H}_3\text{N}_3\text{O}_4$	97.3 [37]	116.7	-19.4
2,4,6-Trinitro-1,3-benzenediol (TNR)	$\text{C}_6\text{H}_3\text{N}_3\text{O}_8$	120.8 [51]	112.2	8.6
1-Chloro-3-nitrobenzene	$\text{C}_6\text{H}_4\text{ClNO}_2$	82.5 [37]	85.7	-3.2
1-Chloro-4-nitrobenzene	$\text{C}_6\text{H}_4\text{ClNO}_2$	74.7 [37]	85.7	-11.0
1-Bromo-2-nitrobenzene	$\text{C}_6\text{H}_4\text{BrNO}_2$	85.2 [37]	85.7	-0.5
1-Bromo-3-nitrobenzene	$\text{C}_6\text{H}_4\text{BrNO}_2$	86.8 [37]	85.7	1.1
1-Iodo-3-nitrobenzene	$\text{C}_6\text{H}_4\text{INO}_2$	83.2 [37]	85.7	-2.5
4-Chloro-3-nitrophenol	$\text{C}_6\text{H}_4\text{ClNO}_3$	111.0 [37]	90.0	21.0
2,5-Dichloro-4-nitroaniline	$\text{C}_6\text{H}_4\text{Cl}_2\text{N}_2\text{O}_2$	114.3 [37]	104.6	9.7
2,6-Dichloro-4-nitroaniline	$\text{C}_6\text{H}_4\text{Cl}_2\text{N}_2\text{O}_2$	109.2 [37]	104.6	4.6
4,5-Dichloro-2-nitroaniline	$\text{C}_6\text{H}_4\text{Cl}_2\text{N}_2\text{O}_2$	109.4 [37]	104.6	4.8
1,2-Dinitrobenzene	$\text{C}_6\text{H}_4\text{N}_2\text{O}_4$	95.5 [37]	98.1	-2.6
1,4-Dinitrobenzene	$\text{C}_6\text{H}_4\text{N}_2\text{O}_4$	94.3 [37]	98.1	-3.8
2,4-Dinitrophenol	$\text{C}_6\text{H}_4\text{N}_2\text{O}_5$	104.6 [36]	102.4	2.2
2,6-Dinitrophenol	$\text{C}_6\text{H}_4\text{N}_2\text{O}_5$	112.1 [36]	102.4	9.7

Table 1 continued

Name	Formula	$\Delta_{\text{sub}}H(\text{exp})/\text{kJ mol}^{-1}$	$\Delta_{\text{sub}}H(\text{cal})/\text{kJ mol}^{-1}$	Dev.
3,4-Dinitrophenol	$\text{C}_6\text{H}_4\text{N}_2\text{O}_5$	123.5 [36]	102.4	21.1
4-Chloro-2,6-dinitroaniline	$\text{C}_6\text{H}_4\text{ClN}_3\text{O}_4$	105.2 [37]	110.3	-5.1
2,4,6-Trinitroaniline (TNA)	$\text{C}_6\text{H}_4\text{N}_4\text{O}_6$	125.3 [51]	122.7	2.6
2-Nitrobenzene-1,3-diol	$\text{C}_6\text{H}_5\text{NO}_4$	74.5 [37]	88.0	-13.5
2-Chloro-4-nitroaniline	$\text{C}_6\text{H}_5\text{ClN}_2\text{O}_2$	102.6 [37]	104.9	-2.3
2-Chloro-5-nitroaniline	$\text{C}_6\text{H}_5\text{ClN}_2\text{O}_2$	101.0 [37]	104.9	-3.9
1,3-Diamino-2,4,6-trinitrobenzene (DATB)	$\text{C}_6\text{H}_5\text{N}_5\text{O}_6$	143.5 [51]	141.9	1.6
3-Methyl-4-nitropyridine 1-oxide	$\text{C}_6\text{H}_6\text{N}_2\text{O}_3$	106.7 [37]	94.3	12.4
2,4,6-Trinitrobenzene-1,3,5-triamine (TATB)	$\text{C}_6\text{H}_6\text{N}_6\text{O}_6$	168.2 [37]	161.1	7.1
<i>N,N</i> -Bis (2,2-dinitropropyl) nitrous amide	$\text{C}_6\text{H}_{10}\text{N}_6\text{O}_9$	110.9 [37]	136.3	-25.4
Trans-1,4,5,8-tetranitro-1,4,5,8-tetraazadecaline (TNAD)	$\text{C}_6\text{H}_{10}\text{N}_8\text{O}_8$	154.2 [50]	139.5	14.7
2-Methyl-2,3,3-trinitropentane	$\text{C}_6\text{H}_{11}\text{N}_3\text{O}_6$	90.8 [37]	77.8	13.0
3,3,6,6-Tetramethyl-1,2,4,5-tetraoxane (DADP)	$\text{C}_6\text{H}_{12}\text{O}_4$	81.9 [52]	66.2	15.7
2,3-Dimethyl-2,3-dinitrobutane	$\text{C}_6\text{H}_{12}\text{N}_2\text{O}_4$	79.5 [37]	65.7	13.8
2,4,6-Trinitrobenzoic acid	$\text{C}_7\text{H}_3\text{N}_3\text{O}_8$	154.7 [50]	152.3	2.4
2-Nitrobenzotrile	$\text{C}_7\text{H}_4\text{N}_2\text{O}_2$	88.1 [37]	92.7	-4.6
3,4-Dinitrobenzoic acid	$\text{C}_7\text{H}_4\text{N}_2\text{O}_6$	129.0 [37]	140.2	-11.2
3-Nitrobenzoic acid	$\text{C}_7\text{H}_5\text{NO}_4$	110.0 [37]	128.1	-18.1
4-Nitrobenzoic acid	$\text{C}_7\text{H}_5\text{NO}_4$	119.7 [37]	128.1	-8.4
3-(5-Nitro-2-furyl)-2-propenal	$\text{C}_7\text{H}_5\text{NO}_4$	97.9 [37]	97.8	0.1
3-Methyl-2,4,6-trinitrophenol	$\text{C}_7\text{H}_5\text{N}_3\text{O}_7$	111.2 [51]	111.6	-0.4
2,4,6- <i>N</i> -Tetranitro- <i>N</i> -methylaniline (tetryl)	$\text{C}_7\text{H}_5\text{N}_5\text{O}_8$	133.8 [51]	130.1	3.7
1-(Chloromethyl)-2-nitrobenzene	$\text{C}_7\text{H}_6\text{ClNO}_2$	96.2 [37]	99.0	-2.8
1-Methyl-2,3-dinitrobenzene	$\text{C}_7\text{H}_6\text{N}_2\text{O}_4$	97.0 [37]	101.9	-4.9
2-Methyl-1,3-dinitrobenzene	$\text{C}_7\text{H}_6\text{N}_2\text{O}_4$	98.3 [37]	101.9	-3.6
2-Methyl-3,5-dinitrophenol	$\text{C}_7\text{H}_6\text{N}_2\text{O}_5$	103.3 [37]	106.2	-2.9
2-Methoxy-4-nitrophenol	$\text{C}_7\text{H}_7\text{NO}_4$	99.4 [37]	98.4	1.0
2-Methoxy-5-nitrophenol	$\text{C}_7\text{H}_7\text{NO}_4$	106.2 [37]	98.4	7.8
4-Methoxy-2-nitrophenol	$\text{C}_7\text{H}_7\text{NO}_4$	90.8 [37]	98.4	-7.6
2,2-Dimethyl-1,1,1,4,4-pentanitropentane	$\text{C}_7\text{H}_{11}\text{N}_5\text{O}_{10}$	103.8 [37]	105.8	-2.0
5-Nitro-1H-indole	$\text{C}_8\text{H}_6\text{N}_2\text{O}_2$	110.5 [37]	111.6	-1.1
1-(3-Nitrophenyl) ethan-1-one	$\text{C}_8\text{H}_7\text{NO}_3$	110.0 [37]	97.3	12.7
2-Methyl-3-nitrobenzoic acid	$\text{C}_8\text{H}_7\text{NO}_4$	119.5 [37]	118.6	0.9
2-Methyl-6-nitrobenzoic acid	$\text{C}_8\text{H}_7\text{NO}_4$	120.0 [37]	118.6	1.4
3-Methoxy-2-nitrobenzoic acid	$\text{C}_8\text{H}_7\text{NO}_5$	141.9 [37]	136.2	5.7
3-Methoxy-4-nitrobenzoic acid	$\text{C}_8\text{H}_7\text{NO}_5$	131.0 [37]	131.9	-0.9
2,4-Dimethyl-1,3,5-trinitrobenzene (TNX)	$\text{C}_8\text{H}_7\text{N}_3\text{O}_6$	129.8 [51]	117.7	12.1
(2,2,2-Trinitroethyl) benzene	$\text{C}_8\text{H}_7\text{N}_3\text{O}_6$	84.1 [37]	83.2	0.9
<i>N,N</i> -Dimethyl-3-nitroaniline	$\text{C}_8\text{H}_{10}\text{N}_2\text{O}_2$	92.7 [37]	97.6	-4.9
<i>N,N</i> -Dimethyl-4-nitroaniline	$\text{C}_8\text{H}_{10}\text{N}_2\text{O}_2$	102.7 [37]	97.6	5.1
2,5-Dimethyl hexane-2,5-dihydroperoxide	$\text{C}_8\text{H}_{18}\text{O}_4$	138.6 [36]	131.1	7.5
5-Nitroquinoline	$\text{C}_9\text{H}_6\text{N}_2\text{O}_2$	94.2 [37]	100.5	-6.3
6-Nitroquinoline	$\text{C}_9\text{H}_6\text{N}_2\text{O}_2$	103.8 [37]	100.5	3.3
5-Nitro-8-hydroxyquinoline	$\text{C}_9\text{H}_6\text{N}_2\text{O}_3$	86.1 [37]	104.0	-17.9
6-Nitroquinolin-5-amine	$\text{C}_9\text{H}_7\text{N}_3\text{O}_2$	136.4 [37]	118.9	17.5
2,4,6-Trimethyl-1,3,5-trinitrobenzene	$\text{C}_9\text{H}_9\text{N}_3\text{O}_6$	103.6 [51]	108.2	-4.6
<i>N,N</i> -Dimethyl-4-nitrobenzamide	$\text{C}_9\text{H}_{10}\text{N}_2\text{O}_3$	115.0 [36]	105.1	9.9
1-(3-Nitrophenyl)-1H-pyrrole-2,5-dione	$\text{C}_{10}\text{H}_6\text{N}_2\text{O}_4$	117.3 [37]	111.6	5.7

Table 1 continued

Name	Formula	$\Delta_{\text{sub}}H(\text{exp})/\text{kJ mol}^{-1}$	$\Delta_{\text{sub}}H(\text{cal})/\text{kJ mol}^{-1}$	Dev.
2-Methyl-8-nitroquinoline	C ₁₀ H ₈ N ₂ O ₂	111.0 [37]	103.5	7.5
1-Nitroadamantane	C ₁₀ H ₁₅ NO ₂	63.6 [37]	67.1	-3.5
2-Nitroadamantane	C ₁₀ H ₁₅ NO ₂	58.0 [37]	67.1	-9.1
(E)-4-((4-Nitrophenyl)amino)pent-3-en-2-one	C ₁₁ H ₁₂ N ₂ O ₃	121.9 [37]	112.1	9.8
(E)-2-Methyl- <i>N</i> -(4-nitrobenzylidene)propan-2-amine	C ₁₁ H ₁₄ N ₂ O ₂	91.1 [37]	108.4	-17.3
(E)- <i>N-tert</i> -Butyl-1-(4-nitrophenyl)methanimine oxide	C ₁₁ H ₁₄ N ₂ O ₃	116.5 [37]	112.7	3.8
1-Nitro-4-(3-nitropentan-3-yl) benzene	C ₁₁ H ₁₄ N ₂ O ₄	110.8 [37]	117.0	-6.2
2,2',4,4',6,6'-Hexanitro-1,1'-biphenyl	C ₁₂ H ₄ N ₆ O ₁₂	171.8 [50]	167.0	4.8
Bis (2,4,6-trinitrophenyl) sulfane	C ₁₂ H ₄ N ₆ O ₁₂ S	173.4 [50]	175.6	-2.2
5,7-Dinitro-1-(2,4,6-trinitrophenyl)-1H-benzo[d] [1-3] triazole	C ₁₂ H ₄ N ₈ O ₁₀	179.7 [50]	165.9	13.8
4,4'-Dinitro-1,1'-biphenyl	C ₁₂ H ₈ N ₂ O ₄	104.6 [37]	118.6	-14.0
4-Hydroxy-4'-nitroazobenzene	C ₁₂ H ₉ N ₃ O ₃	136.8 [37]	118.3	18.5
4-((2,4-Dinitrophenyl)amino) phenol	C ₁₂ H ₉ N ₃ O ₅	155.6 [37]	142.0	13.6
<i>N</i> -(2-Nitrophenyl)- <i>N</i> -phenylamine	C ₁₂ H ₁₀ N ₂ O ₂	101.9 [37]	125.6	-23.7
<i>N</i> -(4-Nitrophenyl)- <i>N</i> -phenylamine	C ₁₂ H ₁₀ N ₂ O ₂	126.2 [37]	125.6	0.6
1-(<i>tert</i> -Butyl)-2-methoxy-4-methyl-3,5-dinitrobenzene	C ₁₂ H ₁₆ N ₂ O ₅	102.9 [37]	98.5	4.4
<i>N</i> -Phenyl 4-nitrobenzaldehyde imine	C ₁₃ H ₁₀ N ₂ O ₂	126.0 [37]	113.7	12.3
1-Amino-5,8-dichloro-4-nitroanthracene-9,10-dione	C ₁₄ H ₆ Cl ₂ N ₂ O ₄	158.2 [37]	139.6	18.6
2,2',4,4',6,6'-Hexanitrostilbene (HNS)	C ₁₄ H ₆ N ₆ O ₁₂	171.6 [50]	174.0	-2.4
1-Nitroanthracene-9,10-dione	C ₁₄ H ₇ NO ₄	108.9 [37]	121.0	-12.1
3,3'-Dimethyl-2,2',4,4',6,6'-hexanitro-1,1'-biphenyl	C ₁₄ H ₈ N ₆ O ₁₂	160.8 [50]	174.5	-13.7
Benzoic peroxyanhydride (or benzoyl peroxide)	C ₁₄ H ₁₀ O ₄	97.9 [37]	91.4	6.5
3-Nitro-4'-(<i>N,N</i> -dimethylamino)-azobenzene	C ₁₄ H ₁₄ N ₄ O ₂	133.9 [37]	125.6	8.3
4-Nitro-4'-(<i>N,N</i> -dimethylamino)-azobenzene	C ₁₄ H ₁₄ N ₄ O ₂	134.3 [37]	125.6	8.7
4-(<i>N,N</i> -Dimethylamino)azobenzene	C ₁₄ H ₁₅ N ₃	117.6 [37]	113.5	4.1
3-Methyl-3'-nitro-4, <i>N,N</i> -dimethylaminoazobenzene	C ₁₅ H ₁₆ N ₄ O ₂	101.7 [37]	116.1	-14.4
4-(<i>N</i> -Ethyl- <i>N</i> -2-hydroxyethylamino)-4'-nitro-2'-chloroazobenzene	C ₁₆ H ₁₇ ClN ₄ O ₃	142.7 [37]	137.2	5.5
4-(<i>N</i> -Ethyl- <i>N</i> -2-hydroxyethylamino)-4'-nitroazobenzene	C ₁₆ H ₁₈ N ₄ O ₃	136.8 [37]	137.4	-0.6
2,4,6-Tri- <i>tert</i> -butylnitrobenzene	C ₁₈ H ₂₉ NO ₂	96.4 [37]	104.7	-8.3

sublimation enthalpies [23]. It was found that $F_{\text{re-pul}} = 1.0$ in substituted nitroaromatics containing small alkyl groups such as methyl groups. Meanwhile, $F_{\text{re-pul}}$ equals 2.0 for bulky groups such as *t*-butyl group. These conditions can be applied if $n_{\text{R}}/n_{\text{NO}_2} \geq 1$, where n_{R} is the number of alkyl groups and $n_{\text{NO}_2} \geq 1$ is the number of nitro groups.

5. *Peroxides*: The presence of C–O–O–C can reduce intermolecular attractions. Thus, for acyclic and cyclic peroxides, $F_{\text{re-pul}}$ is equal to 2.0.
6. *Intermolecular H-Bonding*: Intra- and intermolecular hydrogen bonding play an important role in raising or lowering sublimation enthalpies. Intermolecular H-bonding was described in previous conditions implicitly. But the effect of intramolecular H-bonding should be identified explicitly. Some molecules follow this situation by forming six-membered rings, e.g., 1,3-diamino-2,4,6-trinitrobenzene (DATB), which is sufficiently stable. For these structures, $F_{\text{re-pul}}$ is 0.5.

For those energetic compounds including polynitro arene, polynitro heteroarene, acyclic and cyclic nitramine, nitrate ester, nitroaliphatic, cyclic and acyclic peroxides as well as nitrogen-rich compounds where the above conditions are not satisfied, the values of F_{attract} and $F_{\text{re-pul}}$ equal zero.

The reliability of the new model

Table 4 shows statistical parameters corresponding to M_{rev} , F_{attract} and $F_{\text{re-pul}}$ in model, i.e., Equation (1), which allows comparing the relative mass of the variables in the model. The standard error of model, SE, is an estimate of the deviation of predicted values by the regression model with respect to experimental values; thus, it measures the model error. The standard error of new model is equal to 9.67, where $F = 279.09$ and significance $F = 3.51\text{E}-54$. Standard errors for variables show that whether individual variables are significant in predicting the dependent variable or not, i.e., if the standard error is small relative to the

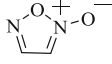
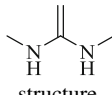
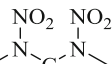
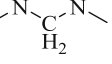
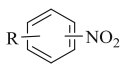
Table 2 Comparison of predicted heats of sublimation/kJ mol⁻¹ of the new method and quantum mechanical computations with the experimental data, in validation set

Name	Formula	$\Delta_{\text{sub}}H(\text{exp})/$ kJ mol ⁻¹	$\Delta_{\text{sub}}H(\text{predicted})/\text{kJ mol}^{-1}$					
			New method		Rice et al. [26]		Byrd et al. [27]	
			Value	Dev.	Value	Dev.	Value	Dev.
Trinitromethane	CHN ₃ O ₆	45.2 [37]	59.0	-13.8	45.2	0.0	58.2	-13.0
Methyldinitramine	CH ₃ N ₃ O ₄	52.0 [36]	50.9	1.1	-	-	-	-
Nitroguanidine (NQ)	CH ₄ N ₄ O ₂	142.7 [51]	152.0	-9.3	-	-	-	-
Hexanitroethane	C ₂ N ₆ O ₁₂	70.7 [37]	99.0	-28.3	82.0	-11.3	77.4	-6.7
1H-1,2,4-triazole	C ₂ H ₃ N ₃	80.7 [37]	86.6	-5.9	-	-	-	-
1-Methyl-1H-tetrazol-5-amine	C ₂ H ₅ N ₅	116.4 [37]	94.7	21.7	-	-	-	-
<i>N,N</i> -Dimethylnitramide	C ₂ H ₆ N ₂ O ₂	41.4 [36]	42.6	-1.2	56.1	-14.7	66.9	-25.5
1,3-Diiodo-1,1,3,3-tetranitropropane	C ₃ H ₂ I ₂ N ₄ O ₈	111.0 [36]	146.3	-35.3	-	-	-	-
1,1,1,2,2-Pentanitropropane	C ₃ H ₃ N ₅ O ₁₀	77.4 [37]	90.7	-13.3	-	-	-	-
1,3,3-Trinitroazetidide (TNAZ)	C ₃ H ₄ N ₄ O ₆	106.2 [50]	104.5	1.7	-	-	-	-
1,3,5-Trinitroso-1,3,5-triazinane (TTT)	C ₃ H ₆ N ₆ O ₃	112.1 [37]	99.7	12.4	93.3	18.8	92.5	19.6
1,3,5-Trinitro-1,3,5-triazinane (RDX)	C ₃ H ₆ N ₆ O ₆	134.3 [51]	142.9	-8.6	102.5	31.8	97.9	36.4
1-Chloro-1,1,3,3-tetranitrobutane	C ₄ H ₅ ClN ₄ O ₈	91.6 [36]	91.6	0.0	-	-	-	-
Bis (2,2,2-trinitroethyl) amine	C ₄ H ₅ N ₇ O ₁₂	80.8 [37]	119.1	-38.3	-	-	-	-
1,1,1,4-Tetranitrobutane	C ₄ H ₆ N ₄ O ₈	99.6 [37]	82.4	17.2	-	-	-	-
4-Nitromorpholine	C ₄ H ₈ N ₂ O ₃	81.6 [36]	88.4	-6.8	-	-	-	-
1,4-Dinitropiperazine	C ₄ H ₈ N ₄ O ₄	111.3 [37]	100.3	11.0	88.7	22.6	89.5	21.8
1,1,1,3,5,5-Heptanitropentane	C ₅ H ₅ N ₇ O ₁₄	111.7 [37]	122.4	-10.7	-	-	-	-
3,5-Dimethyl-4-nitrosopyrazole	C ₅ H ₇ N ₃ O	102.9 [37]	101.7	1.2	-	-	-	-
Pentaerythritol Tetranitrate (PETN)	C ₅ H ₈ N ₄ O ₁₂	150.4 [51]	137.9	12.5	159.8	-9.4	135.1	15.3
2,4-Dichloro-1-nitrobenzene	C ₆ H ₃ Cl ₂ NO ₂	87.8 [37]	85.5	2.3	-	-	-	-
1,3,5-Trinitrobenzene (TNB)	C ₆ H ₃ N ₃ O ₆	107.3 [51]	110.2	-2.9	93.3	14.0	93.7	13.6
2,4,6-Trinitrophenol (Picric acid)	C ₆ H ₃ N ₃ O ₇	105.1 [51]	107.9	-2.8	-	-	-	-
1-Chloro-2-nitrobenzene	C ₆ H ₄ ClNO ₂	80.9 [37]	85.7	-4.8	-	-	-	-
1-Bromo-4-nitrobenzene	C ₆ H ₄ BrNO ₂	86.6 [37]	85.7	0.9	-	-	-	-
4-Chloro-2-nitrophenol	C ₆ H ₄ ClNO ₃	87.6 [37]	90.0	-2.4	-	-	-	-
1,3-Dinitrobenzene	C ₆ H ₄ N ₂ O ₄	87.0 [37]	98.1	-11.1	79.9	7.1	84.1	2.9
2,3-Dinitrophenol	C ₆ H ₄ N ₂ O ₅	96.6 [36]	102.4	-5.8	-	-	-	-
2,5-Dinitrophenol	C ₆ H ₄ N ₂ O ₅	93.4 [36]	102.4	-9.0	-	-	-	-
2-Chloro-4,6-dinitroaniline	C ₆ H ₄ ClN ₃ O ₄	115.0 [37]	117.0	-2.0	-	-	-	-
1-Azido-4-nitrobenzene	C ₆ H ₄ N ₄ O ₂	81.0 [36]	97.0	-16.0	-	-	92.0	-11.0
2-Nitrophenol	C ₆ H ₅ NO ₃	73.3 [37]	83.7	-10.4	71.5	1.8	77.0	-3.7
3-Nitrophenol	C ₆ H ₅ NO ₃	91.2 [37]	90.3	0.9	98.7	-7.5	94.6	-3.4
4-Nitrophenol	C ₆ H ₅ NO ₃	92.4 [37]	90.3	2.1	107.9	-15.5	97.5	-5.1
4-Nitrobenzene-1,2-diol	C ₆ H ₅ NO ₄	121.1 [36]	124.9	-3.8	-	-	-	-
Methyl 5-nitrofuran-2-carboxylate	C ₆ H ₅ NO ₅	104.2 [37]	98.9	5.3	-	-	-	-
2-Nitroaniline	C ₆ H ₆ N ₂ O ₂	89.0 [37]	98.5	-9.5	99.6	-10.6	96.6	-7.6
3-Nitroaniline	C ₆ H ₆ N ₂ O ₂	96.5 [37]	105.2	-8.7	105.8	-9.3	99.6	-3.1
4-Nitroaniline	C ₆ H ₆ N ₂ O ₂	101.4 [37]	105.2	-3.8	-	-	107.9	-6.5
(2,4-Dinitrophenyl) hydrazine	C ₆ H ₆ N ₄ O ₄	124.3 [53]	136.4	-12.2	-	-	-	-
4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane (TEX)	C ₆ H ₆ N ₄ O ₈	123.4 [50]	123.4	0.0	-	-	-	-
2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20)	C ₆ H ₆ N ₁₂ O ₁₂	168.7 [50]	170.7	-2.0	-	-	-	-
<i>N,N</i> -Bis (2,2-dinitropropyl) nitramide	C ₆ H ₁₀ N ₆ O ₁₀	99.2 [37]	106.1	-6.9	-	-	-	-
Bis (2,2-dinitropropyl) amine	C ₆ H ₁₁ N ₅ O ₈	105.4 [37]	102.4	3.0	-	-	-	-

Table 2 continued

Name	Formula	$\Delta_{\text{sub}}H(\text{exp})/\text{kJ mol}^{-1}$	$\Delta_{\text{sub}}H(\text{predicted})/\text{kJ mol}^{-1}$					
			New method		Rice et al. [26]		Byrd et al. [27]	
			Value	Dev.	Value	Dev.	Value	Dev.
Hexamethylene triperoxide diamine (HMTD)	$\text{C}_6\text{H}_{12}\text{N}_2\text{O}_6$	76.2 [54]	82.3	-6.1	-	-	-	-
3-Nitrobenzonitrile	$\text{C}_7\text{H}_4\text{N}_2\text{O}_2$	92.8 [37]	92.7	0.1	-	-	-	-
4-Nitrobenzonitrile	$\text{C}_7\text{H}_4\text{N}_2\text{O}_2$	91.1 [37]	92.7	-1.6	-	-	-	-
2,4-Dinitrobenzoic acid	$\text{C}_7\text{H}_4\text{N}_2\text{O}_6$	135.0 [37]	140.2	-5.2	-	-	-	-
2-Nitrobenzoic acid	$\text{C}_7\text{H}_5\text{NO}_4$	118.7 [37]	128.1	-9.4	-	-	-	-
5-Nitro-1,3-benzodioxole	$\text{C}_7\text{H}_5\text{NO}_4$	97.4 [37]	97.8	-0.4	-	-	-	-
2-Methyl-1,3,5-trinitrobenzene (TNT)	$\text{C}_7\text{H}_5\text{N}_3\text{O}_6$	113.2 [51]	114.0	-0.8	103.8	9.4	100.0	13.2
2-Methoxy-1,3,5-trinitrobenzene	$\text{C}_7\text{H}_5\text{N}_3\text{O}_7$	111.2 [51]	118.3	-7.1	112.5	-1.3	105.8	5.4
(Dinitromethyl) benzene	$\text{C}_7\text{H}_6\text{N}_2\text{O}_4$	76.1 [37]	67.3	8.8	98.3	-22.2	93.7	-17.6
1-Methyl-2,4-dinitrobenzene	$\text{C}_7\text{H}_6\text{N}_2\text{O}_4$	99.6 [37]	101.9	-2.3	88.7	10.9	90.0	9.6
4-Methyl-1,2-dinitrobenzene	$\text{C}_7\text{H}_6\text{N}_2\text{O}_4$	99.6 [37]	101.9	-2.3	-	-	-	-
1-Methyl-4-nitrobenzene	$\text{C}_7\text{H}_7\text{NO}_2$	74.8 [37]	76.5	-1.7	79.9	-5.1	84.9	-10.1
Tris (2,2,2-trinitroethoxy) methane	$\text{C}_7\text{H}_7\text{N}_9\text{O}_{21}$	150.0 [36]	167.1	-17.1	-	-	-	-
2-(2-Nitrophenyl) acetyl chloride	$\text{C}_8\text{H}_6\text{ClNO}_3$	103.6 [37]	106.6	-3.0	-	-	-	-
2-(3-Nitrophenyl) acetyl chloride	$\text{C}_8\text{H}_6\text{ClNO}_3$	109.1 [37]	106.6	2.5	-	-	-	-
2-Chloro-1-phenylethan-1-one	$\text{C}_8\text{H}_7\text{ClO}$	90.7 [37]	94.5	-3.8	-	-	-	-
2,3-Dihydro-6-nitro-1,4-benzodioxin	$\text{C}_8\text{H}_7\text{NO}_4$	100.6 [37]	101.6	-1.0	-	-	-	-
3-Methyl-2-nitrobenzoic acid	$\text{C}_8\text{H}_7\text{NO}_4$	124.4 [37]	118.6	5.8	-	-	-	-
3-Methyl-4-nitrobenzoic acid	$\text{C}_8\text{H}_7\text{NO}_4$	119.3 [37]	118.6	0.7	-	-	-	-
4-Methyl-3-nitrobenzoic acid	$\text{C}_8\text{H}_7\text{NO}_4$	118.6 [37]	118.6	0.0	-	-	-	-
4-Methoxy-3-nitrobenzoic acid	$\text{C}_8\text{H}_7\text{NO}_5$	131.2 [37]	131.9	-0.7	-	-	-	-
2-Ethoxy-1,3,5-trinitrobenzene	$\text{C}_8\text{H}_7\text{N}_3\text{O}_7$	120.5 [37]	122.0	-1.5	-	-	118.0	2.5
5-Nitroindoline	$\text{C}_8\text{H}_8\text{N}_2\text{O}_2$	109.8 [37]	112.2	-2.4	-	-	-	-
8-Nitroquinoline	$\text{C}_9\text{H}_6\text{N}_2\text{O}_2$	106.7 [37]	100.5	6.2	-	-	-	-
(5-Nitrofuran-2-yl) methylene diacetate	$\text{C}_9\text{H}_9\text{NO}_7$	126.0 [36]	118.3	7.7	-	-	-	-
2,4,6-Trimethyl nitrobenzene	$\text{C}_9\text{H}_{11}\text{NO}_2$	78.6 [37]	84.0	-5.4	-	-	-	-
3,3,6,6,9,9-Hexamethyl-1,2,4,5,7,8-hexaoxonane	$\text{C}_9\text{H}_{18}\text{O}_6$	72.5 [52]	86.1	-13.6	-	-	-	-
1-Nitronaphthalene	$\text{C}_{10}\text{H}_7\text{NO}_2$	95.1 [37]	99.5	-4.4	99.6	-4.5	97.9	-2.8
2,2-Dinitroadamantane	$\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_4$	96.4 [37]	79.2	17.2	-	-	90.0	6.4
2-Nitroadamantane-2-carbonitrile	$\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_2$	70.0 [36]	73.8	-3.8	-	-	-	-
Bis (2,4,6-trinitrophenyl)amine (Hexyl)	$\text{C}_{12}\text{H}_5\text{N}_7\text{O}_{12}$	171.6 [50]	186.1	-14.5	-	-	-	-
4-Nitroazobenzene	$\text{C}_{12}\text{H}_9\text{N}_3\text{O}_2$	110.0 [37]	114.0	-4.0	-	-	-	-
2,4-Dinitro- <i>N</i> -phenylaniline	$\text{C}_{12}\text{H}_9\text{N}_3\text{O}_4$	147.6 [37]	137.7	9.9	-	-	-	-
4-Amino-4'-nitroazobenzene	$\text{C}_{12}\text{H}_{10}\text{N}_4\text{O}_2$	123.0 [37]	133.2	-10.2	-	-	-	-
1-(<i>tert</i> -Butyl)-3,5-dimethyl-2,4,6-trinitrobenzene	$\text{C}_{12}\text{H}_{15}\text{N}_3\text{O}_6$	100.4 [37]	106.3	-5.9	-	-	-	-
2-Nitrofluorene	$\text{C}_{13}\text{H}_9\text{NO}_2$	114.2 [37]	109.7	4.5	-	-	-	-
4'-Nitro-2-methylaminoazobenzene	$\text{C}_{13}\text{H}_{12}\text{N}_4\text{O}_2$	134.7 [37]	136.9	-2.2	-	-	-	-
1,4-Dinitroanthracene-9,10-dione	$\text{C}_{14}\text{H}_6\text{N}_2\text{O}_6$	131.0 [37]	133.1	-2.1	-	-	-	-
9-Nitroanthracene	$\text{C}_{14}\text{H}_9\text{NO}_2$	115.4 [37]	112.9	2.5	-	-	-	-
Benzoic (cyclohexyl carbonic) peroxyanhydride	$\text{C}_{14}\text{H}_{16}\text{O}_5$	96.2 [37]	97.4	-1.2	-	-	-	-
1-(4-(<i>tert</i> -Butyl)-2,6-dimethyl-3,5-dinitrophenyl)ethanone	$\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_5$	107.9 [37]	105.5	2.4	-	-	-	-
<i>N</i> -[4-[(2-Hydroxy-5-methylphenyl)azo]phenyl] acetamide (Disperse yellow 3)	$\text{C}_{15}\text{H}_{15}\text{N}_3\text{O}_2$	140.6 [36]	140.4	0.2	-	-	-	-
4-(<i>N,N</i> -Diethylamino)-4'-nitroazobenzene	$\text{C}_{16}\text{H}_{18}\text{N}_4\text{O}_2$	151.5 [37]	133.1	18.4	-	-	-	-
(Peroxybis (methanetetrayl)) hexabenzene	$\text{C}_{38}\text{H}_{30}\text{O}_2$	158.1 [37]	165.8	-7.7	-	-	-	-

Table 3 Summary of correcting functions F_{attract} and F_{repu} account for the presence of different molecular moieties

Molecular moieties	Effect on predicted $\Delta_{\text{sub}}H$		Comment
	F_{attract}	F_{repu}	
–OH and –COOH groups	2.0	–	(a) For one or more –COOH groups (b) For two –OH groups
–NH ₂ , –NH–, and  groups	No. of groups	–	–
 structure	4.7	–	–
	1.0	–	In acyclic nitramines
	2.0	–	In cyclic nitramines
–NO ₂ and >NNO ₂ groups	–	2.6	In nitroaliphatics and the other acyclic nitramines
	–	1.0	For small alkyl groups
structure, $\frac{n_R}{n_{\text{NO}_2}} \geq 1$	–	2.0	For bulky alkyl groups
C–O–O–C group	–	2.0	–
Intermolecular H-Bonding	–	0.5	By formation of 6 membered ring

coefficient, the variable is significant, while if the standard error is larger than the individual coefficient, the variable is much less significant [47]. The P value shows the probability that a parameter estimated from the measured data should have the value which was determined. For P value <0.05 , the effect is significant and the observed effect is not due to random variations. Thus, as seen in Table 4, three variables in Eq. (1) have a highly significant impact as evidenced by their suitable statistical parameters. Moreover, the relative importance of parameters can be confirmed by the correlation coefficients matrix, Table 5,

Table 5 Correlation coefficients matrix for the prediction

Variables	M_{rev}	F_{attract}	F_{repu}	$\Delta_{\text{sub}}H(\text{calc.})$
M_{rev}	1			
F_{attract}	–0.16325	1		
F_{repu}	0.193614	–0.19312	1	
$\Delta_{\text{sub}}H(\text{calc.})$	0.655907	0.46247	–0.43796	1

which was derived for individual parameters and the predicted values of $\Delta_{\text{sub}}H$. Correlation matrix shows all possible pairwise correlation coefficients for a set of variables. In this matrix, regardless the positive or negative signs, low values of correlation coefficients mean that there is no intercorrelation between individual parameters.

Statistical parameters of Eq. (1) were summarized in Table 6 compared to quantum mechanical methods. Magnitude of coefficient of determinations, R^2 , determines that whether regression accounts for the variation or not. Its extreme value is 1.0, which means that the regression accounts for all of the variations and that the correlation is deterministic. Due to the presence of the variety of steric, inter- and intramolecular interactions and uncertainty in the measured heats of sublimation data, which were collected from different sources, the coefficient of determinations are relatively good, i.e., $R^2 = 0.88$ and 0.86 in training and validation sets, respectively. This situation is consistent with large difference between experimental values from various sources, e.g., two different values of heats of sublimation 134.3 and 112.0 kJ mol^{-1} were reported for RDX [36]. As seen in Table 6, R^2 values in external validation set is higher than both quantum mechanical methods, where quantum computation data were available.

The root mean squared deviation, RMS, is a measure of the spread of data around the regression model. It can be used to determine whether the model describes the experimental values with adequate precision. RMS values of Eq. (1) from experiment are 9.5 and 10.0 kJ mol^{-1} , for training and validation sets, respectively. While the RMS deviation of external validation set is 10.5 kJ mol^{-1} that can be compared to 13.7 kJ mol^{-1} , which is the RMS of the method of Byrd et al. [27]. This comparison confirms higher reliability of the new method.

Table 4 Regression coefficients, standard errors, P values, and confidence intervals for the best linear regression model ($R^2 = 0.88$, $\text{SE} = 9.67$, $F = 279.09$, and significance $F = 3.51\text{E}–54$)

	Coefficients	Standard error	P value	Lower bound (95 %)	Upper bound (95 %)
Intercept	52.89	2.603	8.12E–41	47.74	58.05
M_{rev}	0.2689	0.01144	6.26E–47	0.2463	0.2916
F_{attract}	15.13	1.071	2.31E–27	13.013	17.26
F_{repu}	–13.29	0.9444	3.13E–27	–15.16	–11.42

Table 6 Statistical parameters of Eq. (1) for training, validation, and external validation data sets as well as Rice et al. [26] and Byrd et al. [27] methods where computational data were available

Parameter	New model			Quantum mechanical methods	
	Training set (125 data points)	Validation set (88 data points)	External validation set (24 data points)	Rice et al. [26] (20 data points)	Byrd et al. [27] (24 data points)
Coefficient of determinations (R^2)	0.88	0.86	0.83	0.71	0.74
Root mean square error (RMS)	9.5	10.0	10.5	13.8	13.7
Mean absolute error (MAE)	7.6	6.9	8.2	9.5	11.0
Mean absolute percent error (MAPE)	7.4	7.1	9.7	10.4	12.9
Maximum of errors	25.4	38.3	17.2	31.8	36.4

Mean absolute error, MAE, is a linear measure of errors and tells about the average size of errors when negative signs are ignored. For a normal (Gaussian) distribution of errors, the RMS/MAE ratio is ≈ 1.25 [48]. This ratio is 1.25, 1.22, and 1.28 for training, validation, and external validation sets, which means that the error distributions in all data sets are really normal. Mean absolute percent error, MAPE, is used for evaluating the results of model, but also it can make relative comparisons among various methods. This is its biggest advantage as it provides an easy and intuitive way of judging the extent, or importance of errors [49]. Maximum of errors, which determines the worst error in the predictions, is a measure of precision. All of these parameters reveal that the model is free from systematic errors, i.e., unbiased and can predict heats of sublimation with sufficient accuracy and precision.

Conclusions

A new simple method has been introduced for simple and reliable prediction of the heats of sublimation of polynitro arene, polynitro heteroarene, acyclic and cyclic nitramine, nitrate ester, nitroaliphatic, cyclic and acyclic peroxides as well as nitrogen-rich compounds. It is based on three parameters of M_{rev} , F_{attract} , and F_{repul} , which can be found by molecular structure of an energetic compound. The present method gives the simplest and easiest procedure and at the same time gives reliable results with respect to the other available methods that are complex and also require special software.

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