

# A simple correlation for predicting heats of fusion of nitroaromatic carbocyclic energetic compounds

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Received 18 February 2007; received in revised form 24 April 2007; accepted 25 April 2007

Available online 29 April 2007

## Abstract

In this paper, it is shown that heats of fusion of nitroaromatic carbocyclic energetic compounds can be predicted by using some structural parameters. Elemental composition and the contribution of some specific polar functional groups would be needed in the new method. Predicted heats of fusion using the method described herein for 41 nitroaromatic carbocyclic compounds are compared with experimental data. Calculated heats of fusion have a root mean square (rms) deviation of 3.01 kJ/mol and average deviation of 2.35 kJ/mol for these energetic compounds.

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**Keywords:** Heats of fusion; Nitroaromatic carbocyclic compounds; Correlation; Structural parameters

## 1. Introduction

One of the fundamental goals in the field of energetic materials is to develop methods for predicting performance, sensitivity, physical and thermodynamic properties before synthesis. Various simple theoretical and empirical methods can help the chemists to develop systematic and scientific formulations of appropriate futuristic target molecules with desired performance, sensitivity and thermochemical properties. As representative examples of this author's work, some new methods have been recently developed to predict detonation performance at maximum nominal density [1,2], impact and shock sensitivities [3–5], crystal density [6,7] as well as heats of formation [8,9] and detonation [10,11] for some classes of energetic compounds.

Quantum mechanical and group contribution methods are two usual methods, which can be used to predict some thermochemical and physical properties of energetic compounds. Rice et al. [12,13], for example, used the Gaussian 98 suite of quantum chemistry codes with the 6-31G\* basis set and the hybrid B3LYP density functional to determine heats of formation and detonation of energetic compounds. Group contribution methods have been widely used to calculate physical and thermodynamic properties of compounds [14]. They can determine the properties of

a compound by summing the number frequency of each group multiplied by its contribution based on the assumption that the effects of the individual groups are additive. However, many of group contribution methods are of questionable accuracy and limited applicability for organic energetic compounds.

Heat of fusion can be defined as the sum of heat of melting and heats of all polymorph transitions. It represents the work needed for the formation of defects in the crystal lattice. In contrast to the other thermodynamic properties, heats of fusion are not very well estimated by the group contribution method [14–16]. This paper presents a new simple scheme to predict heats of fusion of an important class of energetic compounds namely nitroaromatic carbocyclic compounds. To show the reliability of predicted heats of fusion, the results for 41 (corresponding to 49 measured values) nitroaromatic carbocyclic energetic compounds with different molecular structures are compared with the experimental data.

## 2. Predicting heats of fusion

Thermodynamic and physical properties of polyfunctional compounds are influenced by different molecular interactions. The character and intensity of local interactions, i.e. magnitude, number, distances and orientation of group dipoles within a molecule, are directly connected with the size of a molecule, its conformation, symmetry and with the quantity of the constitu-

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ents present [17]. Zeman and Krupka [18] have found some relationships between heats of sublimation and fusion of some polynitro compounds and lattice energies.

The study of heats of fusion for various nitroaromatic carbocyclic compounds has shown that one can use a new scheme to derive useful equation for predicting heats of fusion. It was found that elemental composition and the contribution of some polar functional groups can influence the values of heats of fusion. Elemental compositions have an important role in predicting thermochemical properties of different classes of energetic compounds such as melting point and gas phase heat of formation of nitramines [19,20]. To establish a new correlation, experimental data of various nitroaromatic carbocyclic were taken from literature. The collected data are listed in Table 1. The results have shown that the following general equation with some adjustable coefficients is suitable for this purpose:

$$\Delta H_{\text{fus}} (\text{kJ/mol}) = w_1 + \sum_{i=1}^4 w_{i+1} b_i + w_6 C_{\text{SPG}} \quad (1)$$

where  $w_1$  to  $w_6$  are adjustable parameters,  $b_i$  the number of used atoms in a compound with general formula  $C_{b_1}H_{b_2}N_{b_3}(O \text{ or } S)_{b_4}$

and  $C_{\text{SPG}}$  is the contribution of specific polar groups. It can be expected that the values of  $C_{\text{SPG}}$  depend on polarity of groups attached to aromatic ring. Experimental data given in Table 1 are used to optimize the values of  $w_1$  to  $w_6$ . The results give the following optimized correlation:

$$\Delta H_{\text{fus}} (\text{kJ/mol}) = 1.197 + 1.681b_1 + 6.793b_3 - 2.143b_4 + 8.526C_{\text{SPG}} \quad (2)$$

Since the contribution of  $w_3$  is small with respect to the other adjustable parameters,  $b_2$  was not included in Eq. (2). As seen in Eq. (2), coefficient of  $C_{\text{SPG}}$  has positive sign, which can increase the value of heat of fusion. This confirms that the existence of polar groups can enhance intermolecular forces. The value of  $C_{\text{SPG}}$  can be determined as follows:

- $C_{\text{SPG}}$  = the number of hydroxyl groups attached to aromatic ring, e.g.  $C_{\text{SPG}} = 2.0$  for 1,3-dihydroxy-2,4,6-trinitrobenzene.
- $C_{\text{SPG}} = 2.0$  for nitroaromatic carbocyclic compounds which have more than two amino ( $-\text{NH}_2$ ) groups attached to aromatic ring, e.g.  $C_{\text{SPG}} = 2.0$  for 1,3,5-triamino-2,4,6-trinitrobenzene (TATB).

Table 1  
Comparison of predicted heats of fusion (kJ/mol) of nitroaromatic carbocyclic compounds with the experimental data

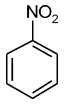
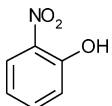
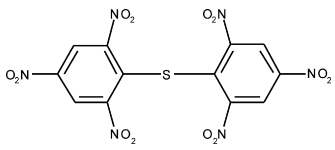
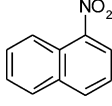
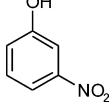
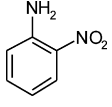
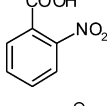
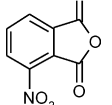
Name	Molecular structure	$\Delta H_{\text{fus}}$ (exp)	$\Delta H_{\text{fus}}$ (cal)	Dev
Nitrobenzene		12.12 [23]	13.79	1.67
2-Nitrophenol		17.45 [23]	20.17	2.73
3-Nitroaniline		23.69 [23]	20.58	-3.11
1-Nitronaphthalene		18.43 [23]	20.51	2.08
3-Nitrophenol		19.20 [23]	20.17	0.98
1-Nitroaniline		16.11 [23]	20.58	4.47
2-Nitrobenzoic acid		27.99 [23]	28.24	0.25
3-Nitrophthalic anhydride		18.40 [23]	19.25	0.85

Table 1 (continued)

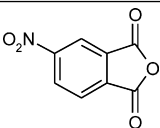
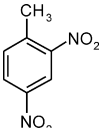
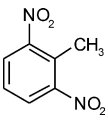
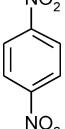
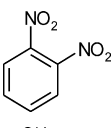
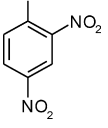
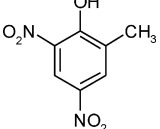
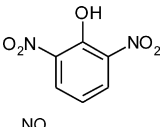
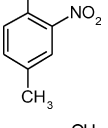
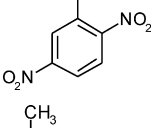
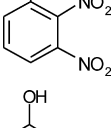
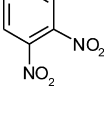
Name	Molecular structure	$\Delta H_{\text{fus}}$ (exp)	$\Delta H_{\text{fus}}$ (cal)	Dev
4-Nitrophthalic anhydride		17.14 [23]	19.25	2.11
1-Methyl-2,4-dinitrobenzene		20.12 [23]	17.98	-2.14
2-Methyl-1,3-dinitrobenzene		19.28 [23]	17.98	-1.30
1,4-Dinitrobenzene		28.12 [23]	24.82	-3.30
1,2-Dinitrobenzene		28.12 [23]	24.82	-3.30
2,4-Dinitrophenol		24.17 [23]	22.68	-1.49
2-Methyl-4,6-dinitrophenol		19.41 [23]	24.36	4.95
2,6-Dinitrophenol		19.58 [23]	22.68	3.10
4-Methyl-1,2-dinitrobenzene		18.83 [23]	17.98	-0.85
2,5-Dinitrophenol		23.73 [23]	22.68	-1.05
1-Methyl-2,3-dinitrobenzene		17.57 [23]	17.98	0.41
3,4-Dinitrophenol		25.38 [23]	22.68	-2.70

Table 1 (continued)

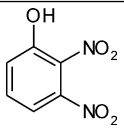
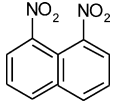
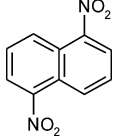
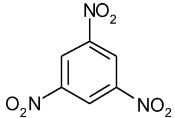
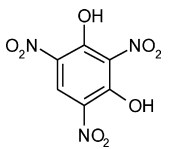
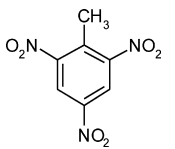
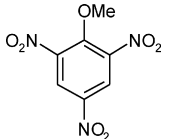
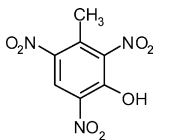
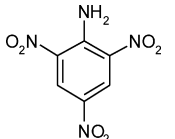
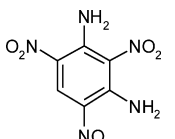
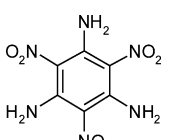
Name	Molecular structure	$\Delta H_{\text{fus}}$ (exp)	$\Delta H_{\text{fus}}$ (cal)	Dev
2,3-Dinitrophenol		26.24 [23]	22.68	-3.56
1,8-Dinitronaphthalene		35.23 [26]	31.55	-3.68
1,5-Dinitronaphthalene		33.03 [26]	31.55	-1.48
1,3,5-Trinitrobenzene		15.69 [21]	18.81	3.12
2,4,6-Trinitroresorcinol		16.74 [22]		2.07
		33.50 [23]	31.51	-1.93
1-Methy-2,4,6-trinitrobenzene		28.80 [21]		2.77
		21.86 [21], 19.58 [21], 21.94 [22], 23.43 [23]	20.49	-1.37, 0.91, -1.45, -2.94
1-Methoxy-2,4,6-trinitrobenzene		19.64 [21,22]	18.34	-1.30
1-Methyl-3-hydroxy-2,4,6-trinitrobenzene		26.74 [21], 26.01 [22]	26.87	0.13, 0.86
1-Amino-2,4,6-trinitrobenzene		28.15 [21]	25.6	-2.55
1,3-Diamino-2,4,6-trinitrobenzene		35.25 [21]	32.39	-2.86
1,3,5-Triamino-2,4,6-trinitrobenzene		56.60 [21]	56.23	-0.37

Table 1 (continued)

Name	Molecular structure	$\Delta H_{\text{fus}}$ (exp)	$\Delta H_{\text{fus}}$ (cal)	Dev
2,4,6-Trinitrobenzoic acid		31.60 [21]	33.25	1.65
1,4,5-Trinitronaphthalene		27.49 [26]	25.53	-1.96
1-(Methylnitramino)-2,4,6-trinitrobenzene		25.85 [21], 22.97 [22]	29.79	3.94, 6.82
2,2',4,4',6,6'-Hexanitrobiphenyl		37.44 [21]	36.41	-1.03
2,2',4,4',6,6'-Hexanitrobibenzyl		43.85 [21]	39.78	-4.07
2,2',4,4',6,6'-Hexanitrodiphenylamine		37.38 [22]	43.21	5.83
2,2',4,4',6,6'-Hexanitrostilbene		40.21 [21]	39.78	-0.43
2,2',4,4',6,6'-Hexanitrodiphenylsulfide		38.00 [21]	34.27	-3.73
2,2',4,4',6,6'-Hexanitrodiphenylsulfone		40.36 [21]	38.51	-1.85
3,3'-Dimethyl-2,2',4,4',6,6'-hexanitrobiphenyl		33.69 [21]	39.78	6.09
rms deviation (kJ/mol)				3.01
Average deviation (kJ/mol)				2.35

- (c)  $C_{SPG}$  has the values 1.0 and 2.0 for the existence at least one  $-C(=O)-O-C(=O)-$  or  $-S(O)_2-$  (sulphone) and  $-COOH$  functional groups attached to aromatic ring, respectively. As representative examples,  $C_{SPG} = 1.0$  for 4-nitrophthalic anhydride and  $C_{SPG} = 2.0$  for 2-nitrobenzoic acid.
- (d)  $C_{SPG} = 1.0$  for disubstituted nitroaromatic compounds that contain only two nitro groups attached to aromatic rings, e.g. 1,8-dinitronaphthalene.

As seen in Table 1, heat of fusion of 41 different nitroaromatic carbocyclic compounds are calculated and compared with the experimental values. Due to uncertainty in heats of fusion data from different sources, e.g. 19.58, 21.86 [21], 21.94 [22] and 23.43 kJ/mol [23] for 1-methyl-2,4,6-trinitrobenzene (TNT),  $R$ -squared value or the coefficient of determination of this correlation is 0.91 [24]. Moreover, due to the existence of the variety of steric, inter- and intramolecular interactions, predicted results by Eq. (2) are remarkable. Since some of data from the NIST Chemistry Web Book [23] have different reported values from different sources, e.g. 12.121, 10.815 and 12.12 kJ/mol are several different reported experimental data for nitrobenzene, the latest reported experimental values of this reference were taken for comparison with the present method. As indicated in Table 1, the estimated heats of fusion of nitroaromatic carbocyclic compounds by new correlation are within  $\pm 5.0$  kJ/mol of 46 measured values and more than  $\pm 5.0$  kJ/mol for remainder three experimental data. A visual comparison of the predictions with experiment is given in Fig. 1. As evident in Fig. 1, the new method shows good agreement with experimental data.

As indicated in Table 1, Eq. (2) gives the same prediction for different isomers. However, deviations of heats of fusion for different isomers are usually small. Two isomers 4-nitro-5-methyl phenol and 2-nitro-5-methyl phenol, for further examples, have

experimental heats of fusion 27.404 and 20.792 kJ/mol [25], respectively. Calculated heat of fusion for these isomers is 21.105 kJ/mol, which lies between two measured values.

### 3. Conclusions

Performance, sensitivity, thermochemical and physical properties of an energetic compound are the essential parameters of somewhat more practical importance to the explosive user. It is not always possible to find measured values of properties for the compounds of interest in the literature. The main intent was to investigate the likelihood of obtaining a simple procedure for calculating heats of fusion of nitroaromatic carbocyclic compounds because it can not very well estimated by the group contribution method [14–16]. The introduced correlation will be very valuable in directing research efforts towards design of energetic organic molecules with desired heat of fusion. The present method may be appealing and the results are very promising because it requires as input only some structural parameters of energetic compounds. Comparison of calculated results with experimental data listed in Table 1 may be taken as appropriate validation of the new procedure for use with nitroaromatic carbocyclic compounds.

### Acknowledgement

I would like to thank the research committee of Malek-ashtar University of Technology (MUT) for supporting this work.

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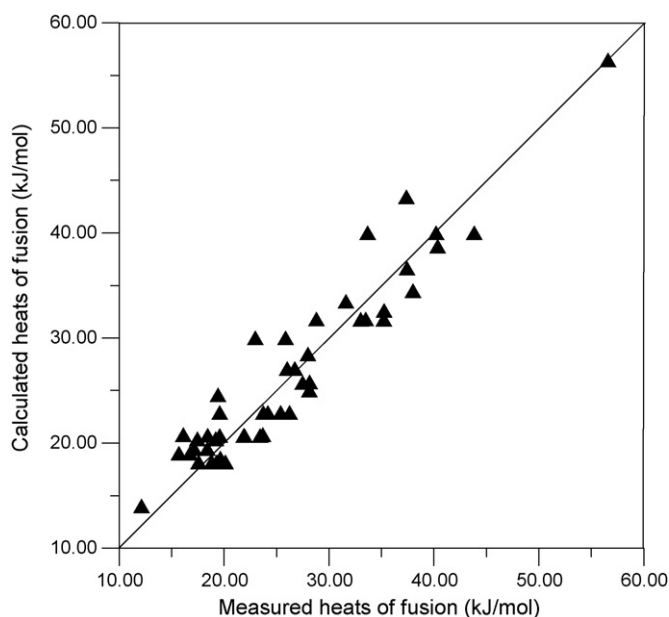


Fig. 1. Predicted heats of fusion of nitroaromatic carbocyclic compounds vs. experimental values. The solid lines represent exact agreement between predictions and experiment. Filled triangles denote calculated results of new method.

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