



Using molecular structure for reliable predicting enthalpy of melting of nitroaromatic energetic compounds

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ABSTRACT

In this work, a reliable simple method has been introduced for predicting enthalpy of melting of nitroaromatic energetic compounds through their molecular structures. This method can be used for a wide range of nitroaromatics including halogenated nitroaromatic compounds. The contribution of hydrogen bonding and polar groups as well as structural parameters can be used to improve the predicted values on the basis of the number of carbon, nitrogen and oxygen atoms. The predicted results show that this method gives reliable prediction of standard enthalpy of melting with respect to the best available methods for different nitroaromatic compounds including high explosives with complex molecular structures.

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1. Introduction

The experimental thermophysical property data of many energetic materials have not been published yet because of their expensive and often hazardous synthesis, testing, and fielding. Elimination of a poor candidate for energetic compounds before investing in synthesis and testing is of great value. The development of various empirical and computational methods to predict thermochemical properties, performance and sensitivity allows such screening upon the conception of a new energetic material.

When the solid and liquid phases are in equilibrium, the free energy of melting is equal to zero. The enthalpy of fusion or melting (ΔH_m) is thus related to the entropy change of melting (ΔS_m) and the melting point temperature (T_m) by

$$\Delta H_m = T_m \Delta S_m \quad (1)$$

Since there is a large variety of steric, inter- and intra-molecular interactions in organic compounds, it is difficult to estimate the enthalpy or entropy of melting at the melting point. Some of new nitroaromatic compounds can be used in various applications such as heat-resistant explosives, high-performance explosives, insensitive high explosives for low-vulnerability munitions, and melt

castable explosives or explosive binders for better performance [1,2].

Zeman and Krupka [3,4] have tried to correlate the impact sensitivity of some polynitro compounds, detected by sound and expressed as the drop energy, with their enthalpy of melting. The enthalpy of melting can represent the work needed for the formation of defects in the crystal lattice. They have found [3,4] that there are some linear logarithmic relationships with very different slopes between the impact sensitivity and enthalpy of melting. They have concluded that the relationships seem to be in accordance with the ideals regarding the decisive role of plastic deformations of the crystal in the shock impact initiation of energetic materials. A simple method has been recently introduced for quick estimation of enthalpy of melting of carbocyclic nitroaromatic compounds [5]. This method is based on the number of carbon, nitrogen and oxygen (or sulfur) atoms as well as the contribution of some polar groups of the compound. Since this model may show relatively large deviations of the predictive results for some halogenated and different isomers of nitroaromatics, it would be necessary to improve it. The purpose of this work is to extend the previous work for improving the overall reliability of predictive results over a wide range of different classes of nitroaromatics. The predicted results are compared with experimental data and the estimated values of the best available predictive methods. It will be shown in the new model that some specific structural parameters can have increasing or decreasing effects in the predicted results on the basis of elemental composition. Some nitroaromatic explosives with complex molecular structures have been tested in the new scheme.

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Table 1

Comparison of the predicted enthalpy of melting (kJ/mol) of nitroaromatic compounds by new method and previous work [5] as well as Jain et al. method [10] with experimental data.

No.	Energetic compound	Exp.	New method	Dev	Previous work	Dev	Jain et al.	Dev
1		30.72 [4]	34.34	3.62	23.85	-6.87	19.39	-11.33
2		40.10 [4]	43.23	3.13	54.28	14.18	29.81	-10.29
3		19.20 [15]	15.27	-3.93	15.47	-3.73	13.03	-6.17
4		10.29 [15]	15.05	4.76	24.24	13.95	23.17	12.88
5		32.64 [15]	27.82	-4.82	20.58	-12.06	18.29	-14.35
6		56.60 [4]	57.53	0.93	56.23	-0.37	28.72	-27.88
7		12.12 [15]	14.08	1.96	13.79	1.67	12.54	0.42
8		17.45 [15]	20.59	3.15	20.17	2.73	16.43	-1.02
9		23.69 [15]	23.87	0.18	20.58	-3.11	16.14	-7.55
10		19.20 [15]	20.59	1.40	20.17	0.98	16.43	-2.77
11		16.11 [15]	19.92	3.81	20.58	4.47	16.14	0.03

Table 1 (Continued)

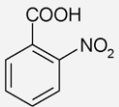
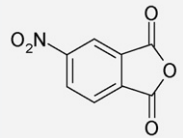
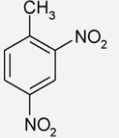
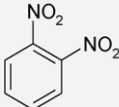
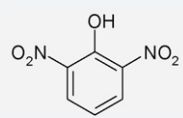
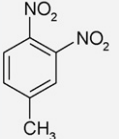
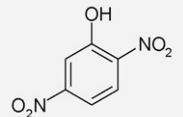
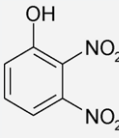
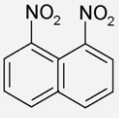
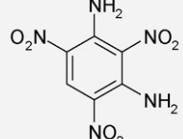
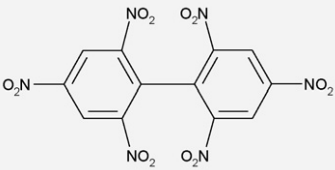
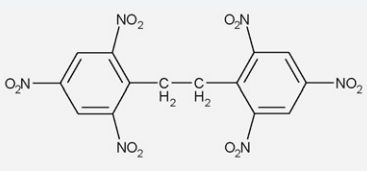
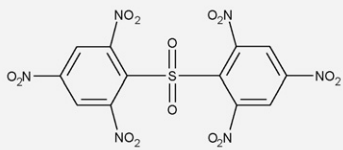
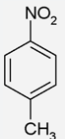
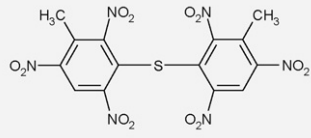
No.	Energetic compound	Exp.	New method	Dev	Previous work	Dev	Jain et al.	Dev
12		27.99 [15]	24.36	-3.63	28.24	0.25	22.27	-5.72
13		17.14 [15]	20.22	3.08	19.25	2.11	18.95	1.81
14		20.12 [15]	18.36	-1.76	17.98	-2.14	15.72	-4.40
15		22.84 [15]	21.11	-1.73	24.82	1.98	15.24	-7.60
16		24.17 [15]	23.68	-0.50	22.68	-1.49	19.12	-5.05
17		19.58 [15]	18.54	-1.03	22.68	3.10	19.12	-0.46
18		18.83 [15]	18.36	-0.47	17.98	-0.85	15.27	-3.56
19		23.73 [15]	23.68	-0.05	22.68	-1.05	19.12	-4.61
20		26.24 [15]	23.68	-2.56	22.68	-3.56	19.12	-7.12
21		35.23 [3]	33.79	-1.44	31.55	-3.68	17.40	-17.83
22		35.25 [4]	35.89	0.64	32.39	-2.86	25.12	-10.13

Table 1 (Continued)

No.	Energetic compound	Exp.	New method	Dev	Previous work	Dev	Jain et al.	Dev
23		37.44 [4]	36.67	-0.77	36.41	-1.03	31.46	-5.98
24		43.85 [4]	39.06	-4.79	39.78	-4.07	36.19	-7.66
25		40.36 [4]	40.42	0.06	41.81	1.45	33.96	-6.40
26		16.00 [15]	15.27	-0.73	15.47	-0.53	13.03	-2.97
27		57.78 [4]	37.63	-20.15	54.86	-2.92	34.92	-22.86
	rms deviation (kJ/mol)			2.50		5.30		7.92

2. Theory

The enthalpy of melting can be assumed to be dependent upon the interactions between the molecular fragments and is therefore equal to the summation of the group values on the basis of group contribution methods [6]. Each molecule can be broken down into defined groups and for each group a standard enthalpy value can be assigned. The sum of all these values gives total enthalpy of melting. Thus, the enthalpy of melting can be calculated by

$$\Delta H_m = \sum n_i m_i \quad (2)$$

where n_i is the occurrence of the group i in the compound and m_i is the contribution of the group i to the enthalpy of melting. Group contribution methods can be used to predict enthalpy of melting for some classes of organic compounds. Some authors have tried to improve these predictive methods through increasing the group contribution values [6–10]. Jain et al. [10] have introduced the 107 group contribution values, which give good results with respect to the other group contribution methods. The calculated enthalpy and entropy of melting can be combined to predict melting points through Eq. (1). For nitroaromatic energetic compounds, group contribution methods give large deviations in some cases.

It was shown that the enthalpy of melting of nitroaromatic carbocyclic energetic compounds can be predicted by using elemental composition and the contribution of some specific polar functional groups [5]. For some cases such as the attachment of tertiary (or secondary) amine to nitroaromatic ring, deviations produced by this method may be large. It will be shown that this model can be mod-

ified to improve its reliability for different classes of nitroaromatic compounds.

3. Results and discussion

For nitroaromatic compounds, the enthalpy of melting depends upon the contribution of the various molecular structure parameters. The magnitude of the contribution of any molecular structure parameter is related to different factors such as its dipole moment, polarizability, hydrogen bond donor and acceptor properties. It also depends on the change in the distance between the structural parameter of a given molecular structure and the structural parameters of its neighboring molecules that accompanies the transition of melting. It was found that reliable prediction of the enthalpy of melting of nitroaromatic energetic compounds can be obtained through suitable combination of elemental composition and some structural parameters. To predict standard enthalpy of melting of nitroaromatic compounds, the number of carbon, nitrogen and oxygen atoms as well as the contribution of some specific structural parameters can be combined as follows:

$$\Delta H_m = z_1 + z_2 n_C + z_3 n_N + z_4 n_O + z_5 C_{SSP} \quad (3)$$

where n_C , n_N and n_O are the number of carbon, nitrogen and oxygen atoms, C_{SSP} is the contribution of some specific structural parameters and z_1 to z_5 are adjustable parameters. Experimental data for 27 nitroaromatics given in Table 1 were used to fit adjustable parameters of Eq. (3). The number of hydrogen or halogen atoms has no notable contribution in this new model because their existence

does not change the coefficient of determination, the r^2 -value, of Eq. (3). Multiple linear regression method [11] was used to find adjustable parameters. Since the equation set is over determined [11], the left-division method for solving linear equations uses the least squares method. The optimized relation has the following

form:

$$\Delta H_m = 3.817 + 1.196n_C + 5.8471n_N - 1.382n_{O_{\leftarrow}} + 7.898C_{SSP} \quad (4)$$

where the enthalpy of melting is in kJ/mol. The factor C_{SSP} can correct the predicted results on the basis of n_C , n_N and n_O . Some

Table 2
Checking the reliability of the predicted enthalpy of melting (kJ/mol) for different classes of nitroaromatic compounds by new method and previous work [5] as well as Jain et al. method [10].

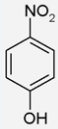
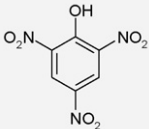
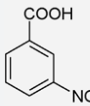
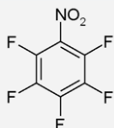
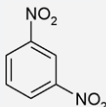
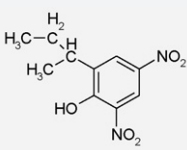
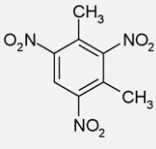
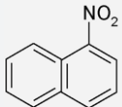
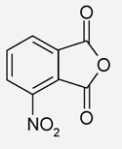
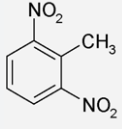
No.	Energetic compound	Exp.	New method	Dev	Previous work	Dev	Jain et al.	Dev
1		30.12 [15]	24.54	-5.58	20.17	-9.94	16.43	-13.69
2		17.41 [4]	21.63	4.22	25.19	7.78	21.81	4.40
3		21.40 [15]	24.36	2.96	28.24	6.84	22.27	0.87
4		11.81 [15]	14.08	2.27	13.79	1.98	12.20	0.39
5		17.35 [15]	21.11	3.76	24.82	7.47	15.24	-2.11
6		21.81 [15]	23.33	1.52	29.41	7.60	22.98	1.17
7		40.87 [4]	38.43	-2.44	22.17	-18.70	18.90	-21.97
8		18.43 [15]	18.86	0.43	20.51	2.08	14.71	-3.72
9		18.40 [15]	20.22	1.82	19.25	0.85	18.95	0.55
10		19.28 [15]	18.36	-0.92	17.98	-1.30	15.27	-4.01

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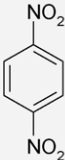
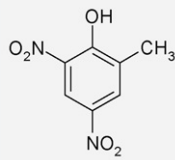
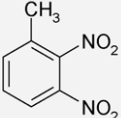
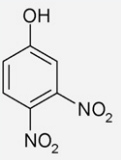
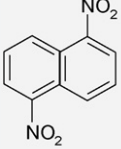
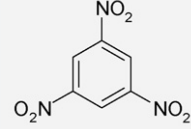
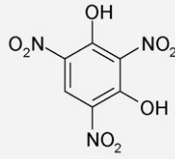
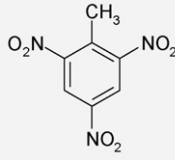
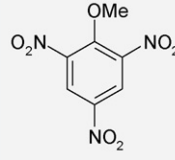
No.	Energetic compound	Exp.	New method	Dev	Previous work	Dev	Jain et al.	Dev
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12		19.41 [15]	19.74	0.33	24.36	4.95	19.61	0.20
13		17.57 [15]	18.36	0.79	17.98	0.41	15.27	-2.30
14		25.38 [15]	23.68	-1.70	22.68	-2.70	19.12	-6.26
15		33.03 [3]	33.79	0.76	31.55	-1.48	17.14	-15.89
16		15.69 [4]	20.24	4.55	18.81	3.12	17.93	2.24
		16.74 [16]		3.50		2.07		1.19
17		33.50 [15]	33.28	-0.22	31.57	-1.93	25.70	-7.80
		28.80 [4]		4.48		2.77		-3.10
18		21.86 [4]	21.44	-0.42	20.49	-1.37	18.42	-3.44
		19.58 [4]		1.86		0.91		-1.16
		21.94 [16]		-0.50		-1.45		-3.52
		23.43 [15]		-1.99		-2.94		-5.01
19		19.64 [4,16]	20.06	0.42	18.34	-1.30	21.03	1.39

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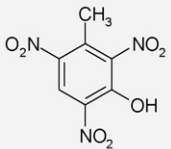
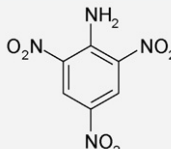
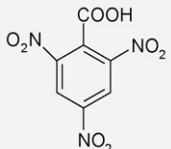
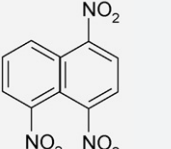
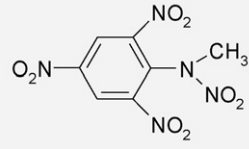
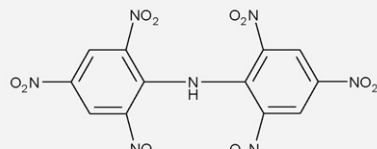
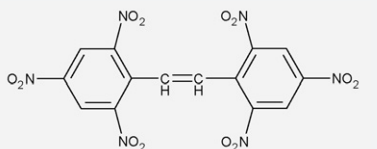
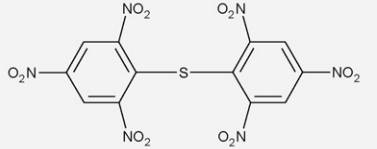
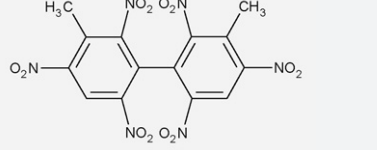
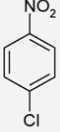
No.	Energetic compound	Exp.	New method	Dev	Previous work	Dev	Jain et al.	Dev
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		26.01 [16]		-3.19		0.86		-3.71
21		28.15 [4]	30.04	1.89	25.60	-2.55	22.30	-3.71
22		31.60 [4]	30.52	-1.08	33.25	1.65	21.53	-6.62
23		27.49 [3]	25.03	-2.46	25.53	-1.96	20.09	-7.40
24		25.85 [4]	22.47	-3.38	29.79	3.94	24.88	-0.97
		22.97 [16]		-0.50		6.82		1.91
25		37.38 [16]	34.62	-2.76	43.21	5.83	35.64	-1.74
26		40.21 [4]	39.06	-1.15	39.78	-0.43	35.75	-4.46
27		38.00 [4]	35.29	-2.71	36.67	-1.33	33.95	-4.05
28		33.69 [4]	39.06	5.37	39.78	6.09	32.43	-1.26

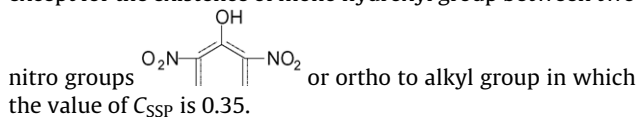
Table 2 (Continued)

No.	Energetic compound	Exp.	New method	Dev	Previous work	Dev	Jain et al.	Dev
29		18.03 [15]	14.08	-3.95	13.79	-4.24	9.21	-8.82
	rms deviation (kJ/mol)			2.48		5.01		6.57

specific functional groups and structural parameters have different effects on the values of the C_{SSP} . For the existence of some polar groups and isomers, the value of C_{SSP} with positive sign can increase the predicted enthalpy of melting on the basis of elemental composition. In contrast, the reverse situation can be observed for the attachment of tertiary and secondary amine as well as Ar–O– to nitroaromatic ring. Two opposite effects of the C_{SSP} on the predicted results on the basis of elemental composition can be specified according to the following situations:

3.1. (a) Increasing effects of C_{SSP}

- (i) Hydroxyl (–OH) groups: The existence of hydrogen bonding has a special impact on the physical and chemical properties of nitroaromatic compounds. It was found that increasing the number of hydroxyl groups attached to aromatic ring can enhance the enthalpy of melting. However, the strong hydrogen bonding leads to much more efficient packing and the attractive forces confining the respective species in the crystal lattice. Thus, C_{SSP} is equal to the number of hydroxyl groups except for the existence of mono hydroxyl group between two



- (ii) Polar groups –C(=O)–C(=O)– and –S(O)₂– as well as –COOH: The values of C_{SSP} are 1.0 and 1.5 for the presence of –C(=O)–C(=O)– (or –S(O)₂–) and –COOH, respectively. The presence of these polar functional groups can increase the predicted values on the basis of elemental composition, which confirms this effect in previous work [5].
- (iii) Amino (–NH₂) groups: It would be expected that an intermolecular hydrogen bonding occurs through the introduction of amino groups. Moreover, the presence of amino groups can enhance the thermal stability of nitroaromatic energetic compounds [1]. Thus, for the presence of amino groups in nitroaromatics, the predicted heats of melting on the basis of elements can be increased. For the presence of one or two amino groups, the value of C_{SSP} is 0.5 except if there is amino group in ortho position of nitro group for mononitro derivatives in which $C_{SSP} = 0.0$. The value of C_{SSP} is 2.5 for the existence of more than two amino groups attached to aromatic ring.
- (iv) Some polar groups in para position of nitro group in benzene ring: The existence of –OH and –NH₂ groups para to nitro group in disubstituted or halogenated benzene ring can increase the enthalpy of melting. The predicted corresponding values of C_{SSP} in parts (i) and (iii) should be replaced by 1.5 and 1.0, respectively. It is obvious that the molecular attractions between adjacent molecules have been increased with respect to parts (i) and (iii) in this situation.
- (v) Two nitro groups: For nitroaromatics with only two nitro groups, the values of C_{SSP} are 0.50 and 1.5 for ortho (or meta) and the other positions, respectively. Since there is an inter-

action between local dipole moments of neighboring atoms or groups, molecular interactions take place that can cause the close distance between molecules in the crystal.

- (vi) More than one alkyl group attached to one benzene ring or two benzene rings that are not attached directly to each other: For specified nitroaromatics with more than one alkyl group, the value of C_{SSP} is $4/n_R$ in which the n_R is the number of alkyl groups. The number of alkyl groups can affect the molecular interactions because increasing the n_R can decrease planarity of the molecule and hence molecular attractions.

3.2. (b) Decreasing effects of C_{SSP}

The attachment of tertiary and secondary amine as well as Ar–O– to nitroaromatic ring can decrease the predicted heat of melting on the basis of elemental composition. The value of C_{SSP} is –1.0 in this situation. The presence of these groups as attachments can decrease planarity of the molecules, which reduces the packing efficiency of molecules in the crystals. Thus, the interaction between local dipole moments of neighboring nitro groups can also be decreased.

The parameter C_{SSP} is equal to zero if the conditions for giving them various values are not met. The coefficient of determination or the r^2 -value of Eq. (4) is 0.93 [11]. The calculated enthalpy of melting of various nitroaromatic compounds given in Table 1 was also compared with previous work [5] and Jain et al. method [10]. As seen in Table 1, the root mean square (rms) value in the new method is 2.50 kJ/mol, which is lower than the rms values from previous work [5] and Jain et al. method [10]. To check the validity of new method for further nitroaromatic compounds, 29 further nitroaromatics (corresponding to 36 measured values) were given in Table 2. According to the rms values from the new model and previous work [5] as well as Jain et al. method [10], the reliability of this work for nitroaromatic energetic compounds is higher than that of best available predictive methods. The predicted results show that this simple method can be easily applied to nitroaromatics with complex molecular structures.

Nitroaromatic energetic compounds will at a certain temperature start to decompose. Crystal structure usually adds to the stability which makes it probable that quite a few start decomposing approaching the melting point; some more will start to decompose during melting and most will decompose above the melting point. Nitroaromatics with high molecular weight can show an increased thermal stability, which is probable from the increase in melting point, since decomposition is much rapid in a melt than in the solid phase [12]. The contribution of elemental composition in Eq. (3) may be consistent with the effect of molecular weight. Moreover, as mentioned in part (iii) for description of increasing effects of C_{SSP} , the presence of amino groups can increase thermal stability of nitroaromatic energetic compounds. For example, 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) exhibits high thermal stability but has no observable melting point [12]. The extra amino group in TATB compared to 1,3-diamino-2,4,6-trinitrobenzene (DATB) increases melting point (>350 °C) with decomposition [12]. Different researches concerning kinetics and

mechanisms of thermal decomposition of nitroaromatic energetic compounds have been reviewed in Refs. [13,14].

4. Conclusions

A new method has been developed for simple and reliable prediction of the enthalpy of melting of nitroaromatic compounds including high explosives. The present method is based on the number of carbon, nitrogen and oxygen atoms as well as the contribution of specific polar groups, which can increase the predicted values on the basis of elemental composition. Some specific structural parameters can also increase or decrease intermolecular interactions. For nitroaromatics, the reliability of the methodology presented here is relatively good compared to the best available methods.

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