

New approach for predicting melting point of carbocyclic nitroaromatic compounds

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Abstract

A simple correlation has been introduced to estimate melting point of carbocyclic nitroaromatic compounds. The methodology assumes that melting point of a carbocyclic nitroaromatic compound with general formula $C_aH_bN_cO_d$ can be expressed as a function of the number of hydrogen and nitrogen atoms as well as the contribution of some specific functional groups and the existence of *ortho* or *para* isomers in disubstituted benzene ring. Predicted melting points using the method described herein and group contribution method of Joback and Reid [K.G. Joback, R.C. Reid, Chem. Eng. Commun. 57 (1987) 233] have the average deviation of 5.0 and 37.6%, respectively, for 60 carbocyclic nitroaromatic compounds. The proposed new method clearly exhibits a much better accuracy.

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Keywords: Melting point; Carbocyclic nitroaromatic compounds; Energetic materials; Correlation

1. Introduction

Prediction of detonation performance, thermal properties and sensitivity of an energetic compound are essential factors prior to its synthesis. Computer codes and empirical methods can help the chemists in the field of energetic materials to improve systematic and scientific formulation of appropriate futuristic target molecules having enhanced performance as well as good thermal stability, impact and friction sensitivity. Suitable energetic materials must combine good performance and physical properties with low vulnerability.

Since the expenditure connected with the development and synthesis of a new energetic material, empirical methods complemented the computer output for desk calculations of performance and physicochemical properties of energetic compounds would be needed. Some new simple methods have been recently introduced for simple evaluation of thermochemical properties of energetic compounds, i.e. heat of formation [1–3], detonation temperature [4–6] and heat of detonation [7].

Group contribution methods are the most comprehensive estimation procedures for boiling point, melting point and vapor pressure, where values assigned to atoms, bonds and their placement in a molecule are used to estimate their contribution to the inherent physicochemical properties of that molecule [8]. A group contribution method expresses the thermodynamic property of a chemical compound as a function of a sum of contributions of small groups of atoms constituting the molecule. As representative examples, some group contribution methods are Joback and Reid [9], Lydersen [10], Ambrose [11], Klinecicz and Reid [12], Lyman et al. [13], Horvath [14], Constantinou et al. [15,16], Prickett et al. [17], Constantinou and Gani [18], Marrero-Morejón and Pardillo-Fontdevilla [19], Marrero and Gani [20]. A simple new procedure has also been recently introduced to predict melting point of selected class of non-nitroaromatic compounds containing nitramines, nitrate esters, nitrate salts and nitroaliphatics energetic compounds [21].

Determination of physicochemical properties of energetic compounds is the essential of somewhat more practical importance to the explosive user. The purpose of this work is to present a new approach for obtaining melting point of carbocyclic nitroaromatic compounds as an important class of organic energetic materials. The major goal of present procedure, apart from being developed as predictive tools, is to provide

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Table 1

Comparison of the results of new method as well as Joback and Reid (J–R) method [9] for calculation of melting point (K) of carbocyclic nitroaromatic compounds with experimental data [23]

No.	Energetic compound	Experiment	New method	%Dev	J–R method	%Dev
1		395	414.40	4.9	750.89	90.1
2		420	442.62	5.4	422.69	0.6
3		386	387.87	0.5	422.69	9.5
4		344	359.57	4.5	422.69	22.9
5		325	310.25	–4.5	350.7	7.9
6		271	271.92	0.3	350.7	29.4
7		288.59	310.25	7.5	350.7	21.5
8		385	398.80	3.6	438.63	13.9
9		318	315.76	–0.7	438.63	37.9
10		368	344.05	–6.5	438.63	19.2
11		363	365.08	0.6	483.04	33.1
12		341	359.57	5.4	506.83	48.6
13		339	359.57	6.1	506.83	49.5
14		329	359.57	9.3	506.83	54.1
15		330	359.57	9.0	506.83	53.6

Table 1 (Continued)

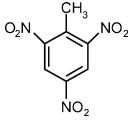
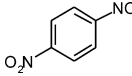

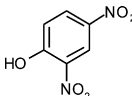
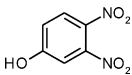

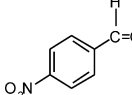
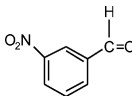


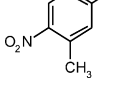


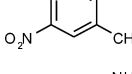
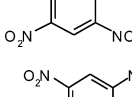
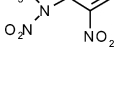
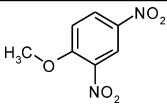
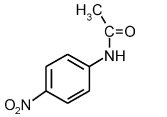
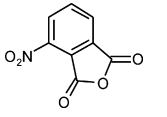
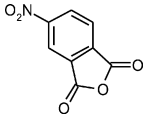
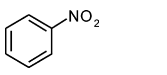
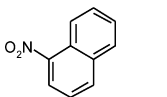
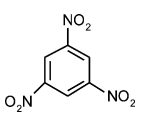
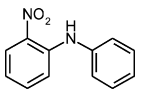
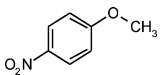
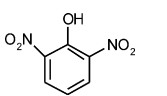
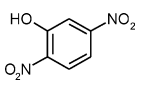
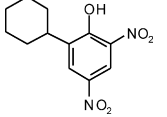
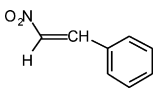
No.	Energetic compound	Experiment	New method	%Dev	J–R method	%Dev
16		355.1	408.90	15.1	662.96	86.7
17		444.2	419.83	-5.5	483.04	8.7
18		387.7	365.08	-5.8	483.04	24.6
19		388	365.08	-5.9	594.76	53.3
20		407	393.38	-3.3	594.76	46.1
21		417	393.38	-5.7	594.76	42.6
22		377.15	370.51	-1.8	392.7	4.1
23		331.65	315.76	-4.8	392.7	18.4
24		288	304.74	5.8	374.49	30.0
25		312.65	315.76	1.0	392.7	25.6
26		282.68	304.74	7.8	374.49	32.5
27		260.9	266.41	2.1	361.97	38.7
28		287.4	304.74	6.0	374.49	30.3
29		301.7	304.74	1.0	374.49	24.1
30		453.05	408.90	-9.7	578.82	27.8
31		402.6	388.85	-3.4	839.04	108.4

Table 1 (Continued)

No.	Energetic compound	Experiment	New method	%Dev	J–R method	%Dev
32		317	299.23	−5.6	398.28	25.6
33		353.65	365.00	3.2	485.94	37.4
34		414.15	410.07	−1.0	511.3	23.5
35		360.25	359.57	−0.2	618.55	71.7
36		436.9	403.31	−7.7	394.44	−9.7
37		333.65	348.55	4.5	394.44	18.2
38		419	410.07	−2.1	511.3	22.0
39		454.9	414.40	−8.9	862.61	89.6
40		343	359.57	4.8	477.48	39.2
41		361.65	359.57	−0.6	477.48	32.0
42		421.65	359.57	−14.7	477.48	13.2
43		369	383.35	3.9	839.04	127.4
44		311.15	310.25	−0.3	372.93	19.9
45		282.35	271.92	−3.7	372.93	32.1
46		309	321.26	4.0	399.49	29.3
47		316.42	343.05	8.4	637.36	101.4

Table 1 (Continued)

No.	Energetic compound	Experiment	New method	%Dev	J–R method	%Dev
48		359.9	359.57	−0.1	529.06	47.0
49		489.1	503.13	2.9	464.56	−5.0
50		436.6	415.58	−4.8	438.29	0.4
51		388	415.58	7.1	438.29	13.0
52		278.9	315.76	13.2	326.91	17.2
53		327.7	310.25	−5.3	417.21	27.3
54		394.2	414.40	5.1	639.17	62.1
55		348.1	348.55	0.1	486.13	39.7
56		327.1	310.25	−5.2	302.89	−7.4
57		336	365.08	8.7	594.76	77.0
58		381	365.08	−4.2	594.76	56.1
59		378.7	337.54	−10.9	682.28	80.2
60		331	310.25	−6.3	346.78	4.8
Average deviation				5.0		37.6

a simple procedure for estimating melting point of organic carbocyclic nitroaromatic compounds. The method will be applied to some carbocyclic nitroaromatic compounds and compared against experimental values as well as Joback and Reid method [9].

2. New approach

The study of melting point for various carbocyclic nitroaromatic organic compounds shows that it is possible to correlate melting point with some specific structural parameters. The

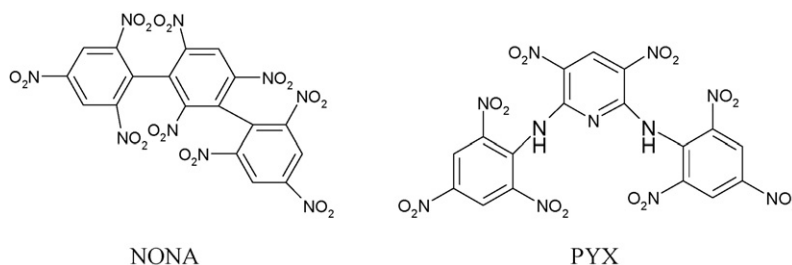


Fig. 1. Molecular structures of NONA and PYX.

results show that four structural parameters are important for a $C_aH_bN_cO_d$ energetic carbocyclic aromatic compound. They are the number of hydrogen and nitrogen atoms as well as the contribution of some specific functional groups and the existence of *ortho* or *para* isomers in disubstituted benzene. To predict melting point of $C_aH_bN_cO_d$ energetic carbocyclic aromatic compounds as a function of four mentioned parameters, the following equation can be used:

$$T_m(\text{K}) = y_1 + y_2b + y_3c + y_4C_{\text{SFG}} + y_5C_{\text{o,p}} \quad (1)$$

where b and c are the number of hydrogen and nitrogen atoms, C_{SFG} the contribution of specific functional group, $C_{\text{o,p}}$ shows the existence of *ortho* or *para* isomers in disubstituted benzene ring and y_1 – y_5 are adjustable parameters which can be found from experimental data given in Table 1. Multiple linear regression method [22] was used to find adjustable parameters. The left-division method for solving linear equations uses the least squares method because the equation set is overdetermined [22]. The results give the following optimized correlation:

$$T_m(\text{K}) = 282.96 - 2.7543b + 46.570c + 94.318C_{\text{SFG}} + 54.752C_{\text{o,p}} \quad (2)$$

The following points should be considered to specify C_{SFG} and $C_{\text{o,p}}$:

- (1) some specific functional groups, such as $-\text{OH}$ and $-\text{NH}_2$ may have different effects in *meta* and *para* position of $-\text{NO}_2$ with respect to *ortho* position. If $-\text{OH}$ and $-\text{NH}_2$ are *ortho* to $-\text{NO}_2$ group, the value of C_{SFG} is zero, but C_{SFG} has the value 0.3 for $-\text{NH}_2$ and $-\text{OH}$ groups in *meta* or *para* position of $-\text{NO}_2$ group. C_{SFG} has the value 1 for the existence of $-\text{COOH}$, $-\text{CON}-$ and $-\text{COO}-$ functional groups. C_{SFG} also has the value -1.2 for the existence of nitramine ($\text{N}-\text{NO}_2$) functional group.
- (2) If aromatic benzene ring contains two substituents, the existence of them in *para* position may increase melting point. The value of $C_{\text{o,p}}$ is 1.0 for *para* disubstituted benzene ring. The existence of alkyl ($-\text{R}$) or alkoxy ($-\text{OR}$) groups in *ortho* position of $-\text{NO}_2$ may cause decreasing melting point. $C_{\text{o,p}}$ has the value -0.7 in this situation.

To demonstrate the present method and test the validity of the correlation, melting point of 60 carbocyclic

nitroaromatic compounds are calculated and compared with the experimental values as well as Joback and Reid [9] method. R -squared values or the coefficients of determination of Eq. (2) is 0.91 [22]. Predicted and experimental melting points using the new method and the percent of error [(predicted–measured)/measured] $\times 100$, are given in Table 1. As indicated in Table 1, the results of new method are in good agreement with experimental values as compared to Joback and Reid [9] method. Since, there are different reported values from different sources, e.g. 355.1, 352, 354, 354.3 and 353.42 K are several different reported experimental data for trinitrotoluene [23], the latest reported values of the NIST Chemistry Web Book were taken to compare the mentioned method with experimental data.

The average percent of deviation in Table 1 for new approach is 5.0%. The estimated melting point by new correlation is within 5.0% of the reported values for 31 energetic compounds, within 5–10% for 25 carbocyclic nitroaromatic compounds and more than 10% for remainder 4 energetic compounds.

The new method can be applied for new carbocyclic nitroaromatic compounds. As representative examples, one can consider two important heat resistant explosives namely 2,2',2'',4,4',4'',6,6',6''-nonanitroterphenyl (NONA) and 2,6-bis(picrylamino)-3,5-dinitropyridine (PYX) that are given in Fig. 1. NONA has a density of 1.78 g cm^{-3} and exceptional heat stability, melting at 713–723 K with decomposition, which together with a low volume of split-off gases render it an interesting material for booster explosives in space technology [24]. PYX is also increasingly being used as a substitute for 2,2',4,4',6,6'-hexanitrostilbene (HNS) and is gradually replacing HNS for most commercial, thermally stable explosive applications. It has crystal density 1.752 g cm^{-3} and melting point 733 K [24]. The calculated melting points by Eq. (2) for two new explosives NONA and PYX are 688 K (%Dev = -3.5 to -4.5) and 776 K (%Dev = 5.9), respectively.

3. Restrictions of the new method

The new correlation has several restrictions that user should consider:

- (a) Eq. (2) can be applied only for carbocyclic nitroaromatic compounds that contain $-\text{NO}_2$ attached to aromatic ring or double bond.

- (b) The new correlation cannot be used for heterocyclic aromatic rings that have more than one heteroatom in aromatic ring, such as triazoles.

4. Conclusions

A new procedure has been developed for simple prediction of melting point of carbocyclic nitroaromatic 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 carbocyclic nitroaromatic compounds. In order to make a quite acceptable comparison of the proposed method with another classical group contribution method, we have calculated the contributions of the group used by Joback and Reid [9]. As compared to Joback and Reid [9] estimation method, the new procedure exhibits an improved accuracy and simple applicability to an important class of energetic materials, namely carbocyclic nitroaromatic compounds. The number of hydrogen and nitrogen and determination of some molecular structure parameters of carbocyclic nitroaromatic compounds are only important factors that would be needed in the novel method. Since prediction of melting point of carbocyclic nitroaromatic compound is readily calculated by a desk calculator, the results of this work are appealing to chemists. The new model gives the simplest and easiest pathway to calculate melting point of carbocyclic nitroaromatic compounds. This reliable method confirms that the accuracy is not necessarily enhanced by greater complexity.

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