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Approximate prediction of melting point of nitramines, nitrate esters, nitrate salts and nitroaliphatics energetic compounds

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Abstract

A simple new procedure is introduced to predict melting point of selected class of energetic compounds containing nitramines, nitrate esters, nitrate salts and nitroaliphatics energetic compounds. The number of nitrogen and oxygen as well as the number of nitramine group and the contribution of some specific functional groups would be needed in the new method. Energetic compounds should contain at least one of the functional groups including N–NO_2, C–ONO_2 or nonaromatic C–NO_2. Calculated melting point for 33 nitramines, nitrate esters, nitrate salt and nitroaliphatics are compared with experimental data. Predicted melting points have average deviation of 5.4% for these energetic compounds.

Keywords: Melting point; Nitramines; Nitrate esters; Nitrate salts; Nitroaliphatic compounds

1. Introduction

Determination of performance and physical properties of a new energetic compound are very important to chemist and energetic material user. The performance of new energetic materials can be evaluated by thermochemical computer codes such as CHEETAH [1]. Moreover, various empirical methods exist so that they complemented the computer output related to detonation performance [2]. Some new simple methods have been recently introduced for simple evaluation thermochemical and important properties of energetic compounds, which contain detonation temperature [3–5], heat of detonation [6,7], Gurney velocity [8], specific impulse [9,10], impact sensitivity [11,12] and heat of formation [13–15].

To estimate the properties of organic compounds, group-contribution methods such as those given by Joback and Reid [16], Lydersen [17], Ambrose [18], Klincewicz and Reid [19], Lyman et al. [20], and Horvath [21] can be used. The property of a compound is a function of structurally dependent parameters in these methods, which are determined by summing the frequency of contribution of each group occurring in the molecule. Many of these methods are of questionable accuracy and limited applicability for organic energetic compounds.

In contrast to the other physicochemical properties, melting points are not very well estimated by the group contribution method [22–24]. Moreover, there is no reliable method for predicting melting points of energetic compounds. The paper presents a new simple scheme for obtaining some important classes of energetic compounds containing nitramines, nitrate esters, nitrate salts and nitroaliphatics materials. The main intent was to investigate the likelihood of obtaining a simple procedure for calculating fusion temperature of mentioned energetic materials. To show the reliability of predicted melting points, the results for 33 well-known and two new energetic compounds are compared with the measured data. The introduced correlation will be very valuable in directing research efforts towards design of energetic organic molecules with desired melting point.

2. Development of new method

The group-contribution method for the estimation method of physical properties of pure compounds proposed by Joback and Reid [25] is popular among the other group-contribution methods. The melting points T_m of pure organic compounds estimated from the Joback and Reid method can be expressed by

$$T_{\mathrm{m}}\,(\mathrm{K}) = 122.5 + \sum N_i C_{\mathrm{m}i} \qquad (1)$$

where N_i is the number of groups of type i and $C_{\mathrm{m}i}$ is the group contributions of the melting points resulting from the

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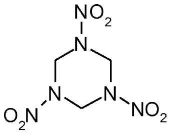
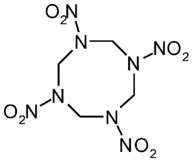
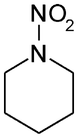
group *i* of the molecule. Although some developments such as method of Xu and Yang [26,27] were used for estimating boiling and melting points of organic compounds, no reliable methods are now available to estimate freezing point of organic compounds. One may use group-contribution methods for a very approximate guess.

Since there are no available methods for obtaining melting point of different classes of energetic materials, one can use a new scheme to derive useful equation for some classes of energetic materials. The study of melting point for various some important classes of energetic compounds containing nitramines, nitrate esters, nitrate salts and nitroaliphatics materials shows that it is possible to express their melting point as a function of elemental composition as well as some special structural parameters and functional groups. To investigate the important structural factors, experimental data of various $C_aH_bN_cO_d$ nitramines, nitrate esters, nitrate salts and nitroaliphatics, which are listed in Table 1, were used. The results show that the follow-

Table 1
Comparison of predicted melting point (K) of nitramines, nitrate esters, nitrated salts and nitroaliphatics energetic compounds with the experimental data

No.	Energetic compound	Experiment[a]	New method	%Dev
1	$CH_3CH_2ONO_2$	178.6	187.65	5.1
2	$CH_3CH(ONO_2)CH_3$	190.81	187.65	−1.7
3	CH_3ONO_2	190.81	187.65	−1.7
4	$O_2NOCH_2CH_2CH_2CH_2ONO_2$	285	257.86	−9.5
5	$O_2NOCH_2CH_2CH_2CH_2CH_2ONO_2$	256.6	257.86	0.5
6	$CH_3CH(ONO_2)CH_2CH_2ONO_2$	253.4	257.86	1.8
7	$CH_3CH(ONO_2)CH_2CH(ONO_2)CH_3$	254.7	257.86	1.2
8	$O_2NOCH_2CH(ONO_2)CH_2ONO_2$	286	293.73	2.7
9	$(O_2NOCH_2)_4C$	413	398.29	−3.6
10	$CH_3(C{=}O)NH_3NO_3$	361	380.03	5.3
11	$(C_6H_5)_4NNO_3$	387.2	355.25	−8.3
12	$[CH_3(CH_2)_6]_4NNO_3$	345	355.25	3.0
13	$[CH_3(CH_2)_3]_4NNO_3$	392.2	355.25	−9.4
14	$[CH_3(CH_2)_5]_4NNO_3$	345	355.25	3.0
15		478.5	472.80	−1.2
16		548	556.91	1.6
17	$(CH_3)_2NNO_2$	345.45	304.58	−11.8
18		267.65	304.58	13.8
19	$C_6H_5NHNO_2$	319.15	304.58	−4.6
20	$CH_3C(CH_2OH)_2NO_2$	424	418.50	−1.3
21	$(O_2N)_3CC(NO_2)_3$	420	424.38	1.0
22	$HOCH_2C(CH_3)_2NO_2$	361.7	393.72	8.9
23	$(O_2N)_3CH$	292	253.74	−13.1
24	$(CH_3)_3CNO_2$	298.65	300.25	0.5
25	$(CH_3)_2C(NO_2)_2$	326	311.34	−4.5
26	$O_2NCH_2CH_2NO_2$	251.8	242.65	−3.6
27	CH_3NO_2	244.6	231.56	−5.3
28	$(CH_3)_2CHCH_2NO_2$	196.3	197.21	0.5
29	$CH_3CH_2CH_2NO_2$	169.16	197.21	16.6
30	$CH_3CH_2CH_2NO_2$	183.63	197.21	7.4
31	$CH_3CH_2CH_2CH_2NO_2$	191.82	197.21	2.8
32	$(CH_3)_2CHNO_2$	181.83	197.21	8.5
33	$C(NO_2)_4$	287.05	333.52	16.2
Average deviation				5.4

[a] Experimental data taken from NIST Chemistry Web Book [29] so that references for individual molecules are given therein.