



A new method for predicting the heats of combustion of polynitro arene, polynitro heteroarene, acyclic and cyclic nitramine, nitrate ester and nitroaliphatic compounds

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Molecular structure

Safety

ABSTRACT

A new method is presented for estimating the gross and net heats of combustion of important classes of energetic compounds including polynitro arene, polynitro heteroarene, acyclic and cyclic nitramine, nitrate ester and nitroaliphatic compounds. Elemental compositions as well as the presence of some specific polar groups and molecular fragments are important parameters in the new model. The novel method can be easily used for any complex organic compounds with at least one nitro, nitramine or nitrate functional groups by which the predictions of their heats of combustion by the available methods are inaccurate or difficult. The predicted results show that this method gives reliable predictions of heats of combustion with respect to group additivity method and computed values based on atom-type electrotopological state indices for several energetic compounds where the models can be applied.

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1. Introduction

Organic compounds with energetic groups such as nitroaromatic compounds are hazardous materials, which can decompose, ignite and explode by heat and impact [1]. Predicting their thermochemical properties are necessary for safe handling, storage, transport and process design before synthesis. Considerable efforts in the field of energetic materials have been focused on the development of suitable models for reliable predictions of their properties. For example, two new methods have been recently introduced to predict the enthalpy and entropy of fusion of nitroaromatic compounds [2,3]. Furthermore, it is possible to design high-energy density materials with high performance and/or decreased sensitivity with respect to thermal, shock, friction sensitivity and electrostatic discharge [4–8].

The heat of combustion of a specified substance is the heat evolved when it is converted to the standard oxidation products by means of molecular oxygen [9]. It is an important property,

which can be used for reactive materials to estimate the potential fire hazards of chemicals once they ignite and burn. The gross heat of combustion is normally determined by the oxygen bomb calorimeter method in which the water is considered in the liquid state. Meanwhile, the net heat of combustion is calculated from the gross heat of combustion by assuming the formation of water is in a gaseous state.

Prediction of the heat of combustion is suitable for computer implementation in applications such as hazard evaluation [10]. A simple prediction model has been developed by Cardozo [11] to relate the length of chain and heat of combustion based on 1168 organic compounds. Cardozo's method [11] cannot be applied for polynitroheteroarenes, acyclic and cyclic nitramines as well as energetic compounds with nitrate functional groups because group correction factors have not been specified for the compounds containing N-NO₂ and O-NO₂ functional groups and molecular fragments in polynitroheteroarenes. Seaton and Harrison [10] have assumed some combustion products for compounds or mixtures of compounds composed of any of 71 elements to estimate the heats of combustion. Their method was based on the Benson method [12] for predicting the heat of formation, which is considered to be too complex for manual calculations. Since energetic compounds are frequently in the solid state at 298 K, suitable new group contri-

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bution and quantum mechanical methods for calculating heat of formation or heat of sublimation can be used to give more reliable predictions [13–16]. However, the tedious calculation procedures by mentioned methods complicate, indirectly, the prediction of heats of combustion.

For organosilicon compounds, Hshieh [9] developed two empirical equations to predict the gross and the net heats of combustion of them on the basis of the atomic contribution method. Hshieh and coworkers [17] have also used the atomic contribution method to develop two other empirical equations for predicting the gross

Table 1

Comparison of the predicted the gross heats of combustion (kJ/mol) of polynitro arene, polynitro heteroarene, acyclic and cyclic nitramine, nitrate ester and nitroaliphatic compounds by the new method with the experimental data.

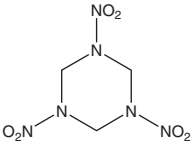
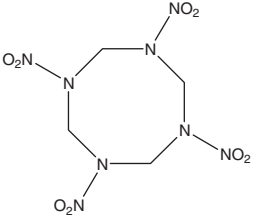
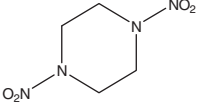
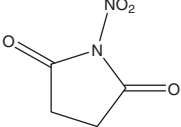
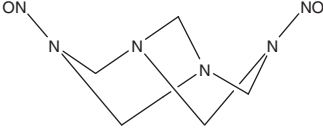
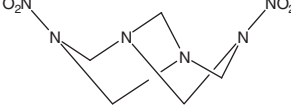
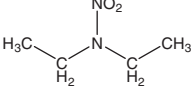
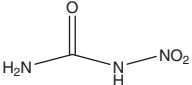
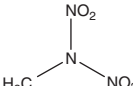
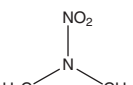
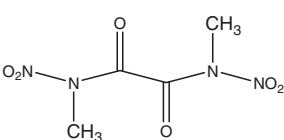
No.	Molecular structure	$-\Delta_c H^\theta(\text{Exp})$	$-\Delta_c H^\theta(\text{Pred})$	Dev
1		2120 [25]	2151	-31
2		2820 [25]	2868	-48
3		2664 [25]	2710	-46
4		1828 [25]	1819	9
5		3448 [26]	3698	-69
6		3629 [26]	3562	-115
7		2897 [25]	2850	47
8		541.4 [25]	629	-88
9		823.8 [25]	799	25
10		1570 [25]	1574	-4
11		2126 [25]	2117	9

Table 1 (Continued)

No.	Molecular structure	$-\Delta_c H^\theta(\text{Exp})$	$-\Delta_c H^\theta(\text{Pred})$	Dev
12		2962 [25]	2981	-19
13		1582 [25]	1482	100
14		2417 [25]	2438	-21
15		2031 [25]	2006	25
16		2696 [25]	2644	52
17		574.5 [25]	581	-7
18		1210 [25]	1219	-9
19		955 [25]	1013	-58
20		2249 [25]	2219	30
21		1846 [25]	1857	-11
22		1361.6 [22]	1357	5
23		2013.4 [22]	1995	19
24		2000.7 [22]	1995	6
25		2667.8 [22]	2633	35
26		2652.7 [22]	2633	20
27		3324.2 [22]	3270	54

Table 1 (Continued)

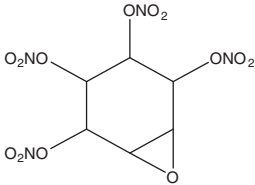
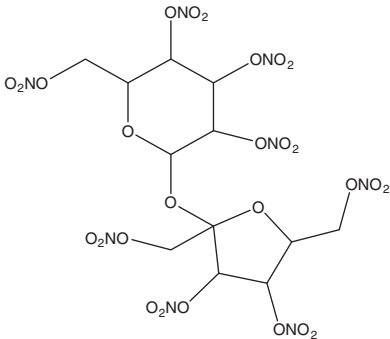
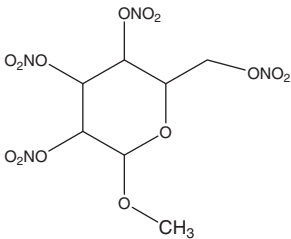
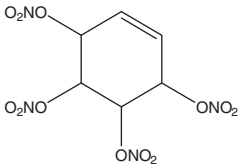
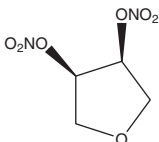
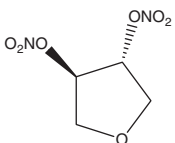
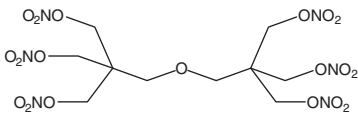
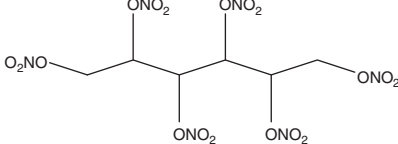
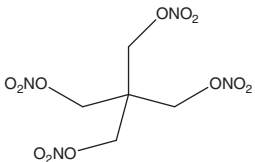
No.	Molecular structure	$-\Delta_c H^\theta(\text{Exp})$	$-\Delta_c H^\theta(\text{Pred})$	Dev
28		2774 [25]	2716	58
29		5394.4 [25]	5584	-189
30		3357.9 [25]	3505	-147
31		2831 [25]	2784	47
32		2025.5 [25]	2072	-46
33		2045.5 [25]	2072	-26
34		5250.5 [25]	5294	-44
35		2807 [25]	2811	-4
36		2572.4 [25]	2585	-13

Table 1 (Continued)

No.	Molecular structure	$-\Delta_c H^\theta$ (Exp)	$-\Delta_c H^\theta$ (Pred)	Dev
37		2205.2 [25]	2015	190
38		2175.7 [25]	2153	23
39		2200 [25]	2221	-21
40		2886.5 [25]	2859	28
41		3454 [25]	3429	25
42		2995 [25]	2997	-2
43		2729.8 [25]	2723	7
44		3633 [25]	3634	-1
45		2175.7 [25]	2153	23
46		2814 [25]	2791	23
47		3161.9 [25]	3155	7
48		1529 [25]	1515	14
49		3012 [25]	2997	15
50		1743 [25]	1721	22

Table 1 (Continued)

No.	Molecular structure	$-\Delta_c H^\theta$ (Exp)	$-\Delta_c H^\theta$ (Pred)	Dev
51		3035 [25]	2997	38
52		2377 [25]	2359	18
53		2387 [25]	2359	28
54		2811 [25]	2791	20
55		2311 [25]	2153	158
56		1959 [25]	1927	32
57		3777.8 [26]	3646	132
58		1540 [25]	1654	-114
59		5511 [25]	5402	109
60		1559 [25]	1574	-15
61		1875 [25]	1857	18
62		3440 [25]	3499	-59
63		1123.3 [25]	1083	40
64		2261 [25]	2291	-30
65		1966 [25]	1927	39
66		3361 [25]	3281	80

Table 1 (Continued)

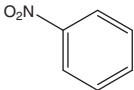
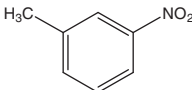
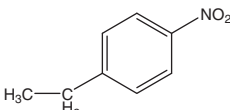
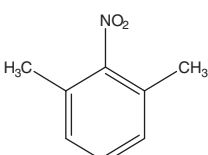
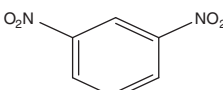
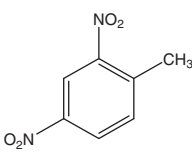
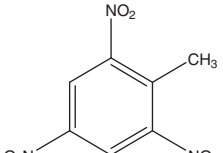
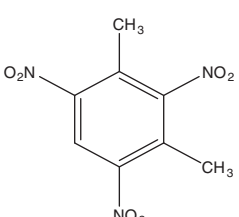
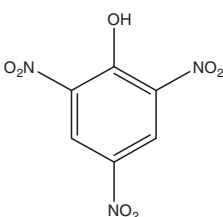
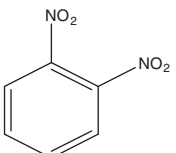
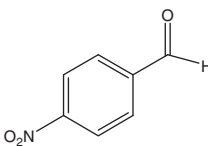
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69		4379 [22]	4377	2
70		4384 [22]	4377	6
71		2910 [22]	2892	18
72		3551 [22]	3530	21
73		3389 [22] 3395 [27]	3392	-3 3
74		4044 [22]	4030	14
75		2560 [22] 2570 [25]	2517	43 53
76		2931 [25]	2892	39
77		3318 [25]	3381	-63

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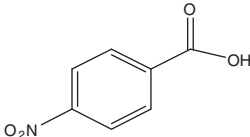
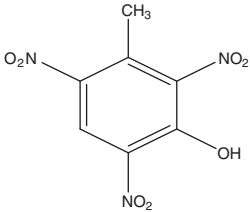
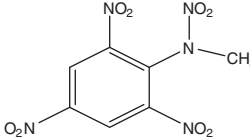
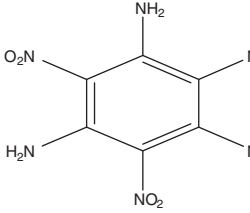
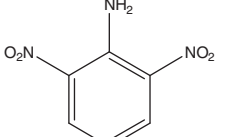
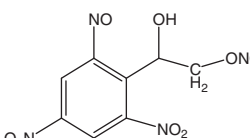
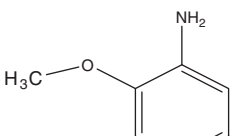
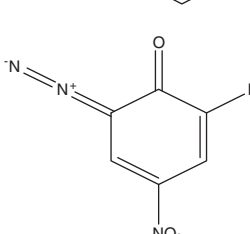
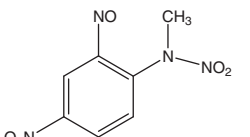
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80		3500 [25]	3472	28
81		3079 [25]	3169	-90
82		3025 [25]	3110	-85
83		3718 [25]	3756	-38
84		3666 [25]	3818	-152
85		2775 [25]	2820	-45
86		3638 [25]	3610	28

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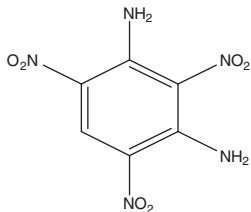
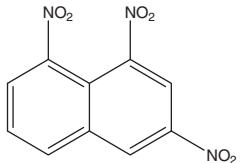
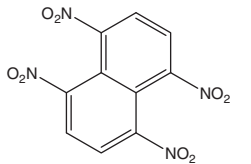
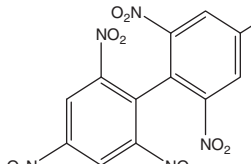
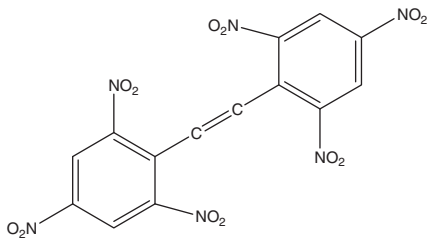
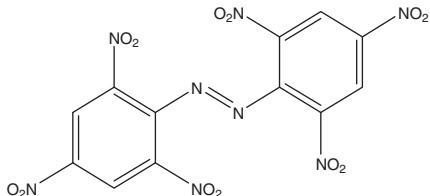
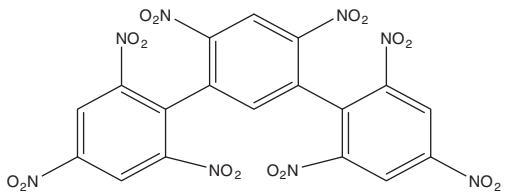
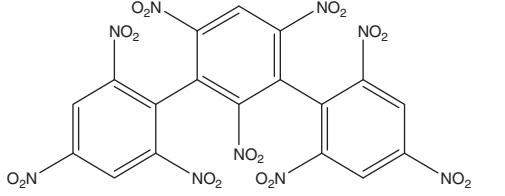
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87		2974[27]	2952	22
88		4676[25]	4647	29
89		4556[27]	4509	47
90		5350[27]	5290	60
91		6438[27]	6346	93
92		5573[27]	5505	68
93		7996[27]	7963	34
94		7905 [27] 7930 [25]	7825	81 105

Table 1 (Continued)

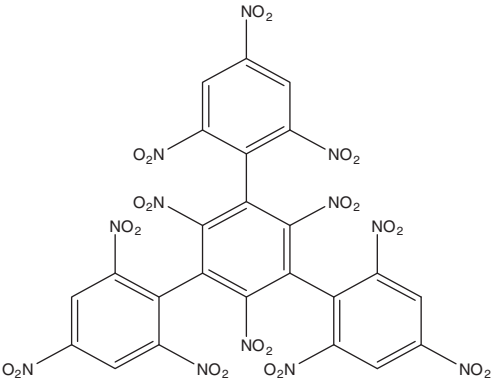
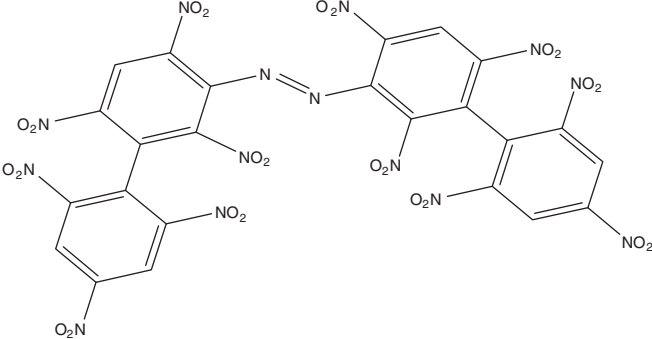
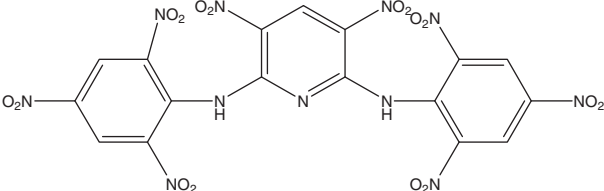
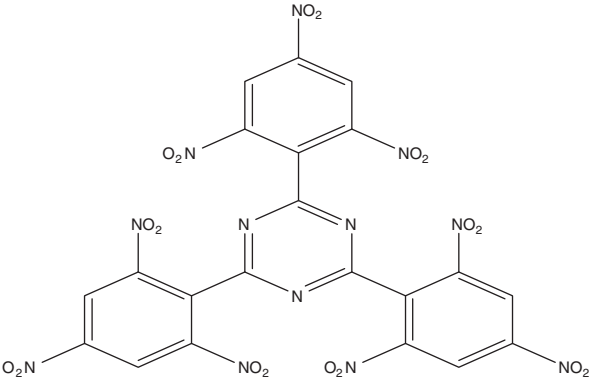
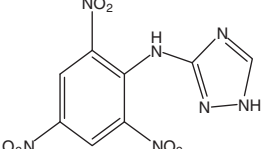
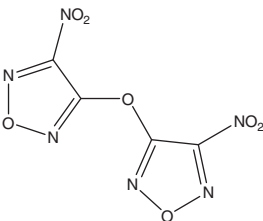
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96		10,779 [27]	10,754	26
97		7769 [27]	7739	29
98		9431 [27]	9512	-81
99		4011 [25]	4003	7
100		1878 [22]	1843	35

Table 1 (Continued)

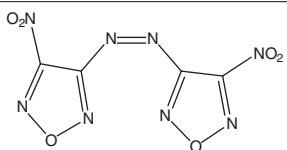
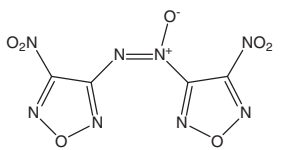
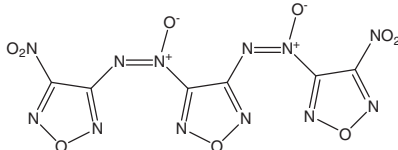
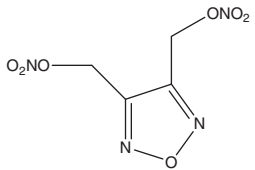
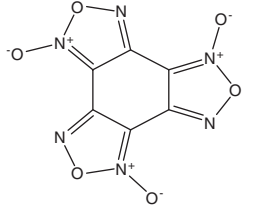
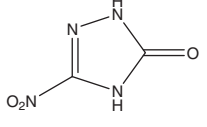
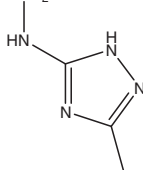
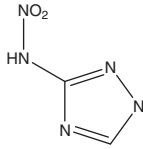
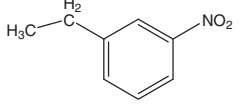
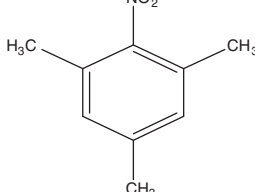
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101		2276 [22]	2305	-29
102		2219 [22]	2237	-18
103		3451 [25]	3368	83
104		2098 [25]	2067	31
105		2960 [27]	2927	33
106		943.4 [25]	1045	-102
107		1948 [25]	1968	-20
108		1328 [25]	1330	-2
109		4386 [22]	4377	8
110		5008 [22]	5015	-7

Table 1 (Continued)

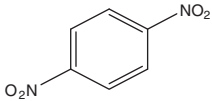
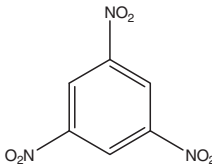
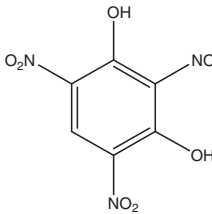
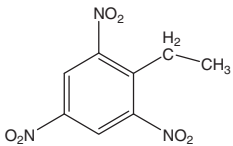
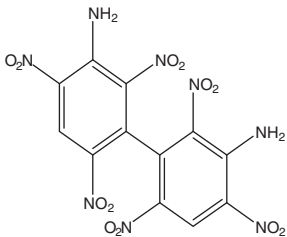
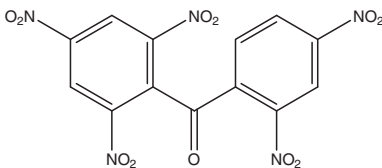
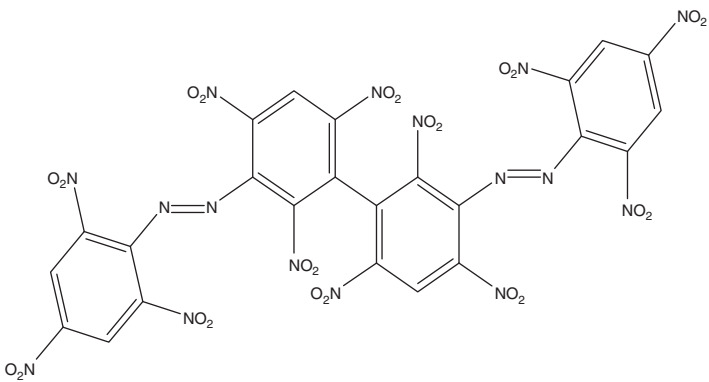
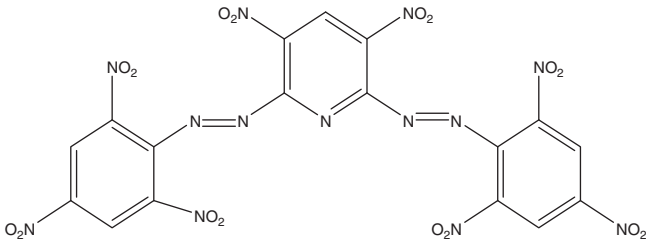
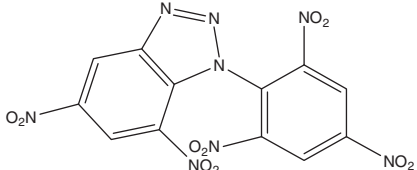
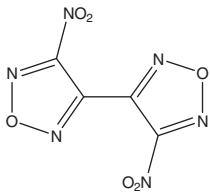
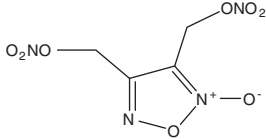
No.	Molecular structure	$-\Delta_c H^\theta$ (Exp)	$-\Delta_c H^\theta$ (Pred)	Dev
111		2902 [22]	2892	10
112		2746 [22]	2755	-9
113		2322 [22]	2382	-59
114		4077 [25]	4030	47
115		5554 [27]	5487	68
116		5714 [27]	5778	-64
117		11,091 [27]	10,969	122
118		8015 [27]	8151	-136

Table 1 (Continued)

No.	Molecular structure	$-\Delta_c H^\theta$ (Exp)	$-\Delta_c H^\theta$ (Pred)	Dev
119		5558 [25]	5640	-82
120		1995 [22]	1911	83
121		2102 [25]	2178	-76
rms deviation (kJ/mol)				60

and net heats of combustion of organic polymers. Equations of Hshieh and coworkers [9,17] have the advantage that only elemental compositions of organosilicon compounds and polymers are input parameters. Although the two models developed by Hshieh and coworkers [9,17] are very simple and easy to apply, their models are only applicable to the organosilicon compounds and polymers.

Quantum mechanical methods can also be used to calculate the heats of combustion. For example, Kondo et al. [18] calculated the heats of formation for several flammable gases by the Gaussian-2 (G2) and/or G2MP2 method to obtain their heats of combustion and related constants for evaluating the combustion hazards. Quantum mechanical methods require special complex software and high speed computers.

Quantitative structure–property relationship (QSPR) models can also be used to predict heat of combustion of organic compounds. Gharagheizi [19] performed a QSPR study to develop a simple model for prediction of standard net heat of combustion of pure chemicals. He used genetic algorithm based multivariate linear regression (GA-MLR) to obtain a four parameters multi-linear equation. Gharagheizi's model requires special software to obtain four complex molecular descriptors. Cao et al. [20] introduced another suitable QSPR based on the atom-type electrotopological state (E-state) indices and artificial neural network (ANN) technique to predict standard net heat of combustion of organic compounds. Although model of Cao et al. [20] is simpler to apply with respect to Gharagheizi's model, calculation of the atom-type E-state indices for polynitro arene and polynitro heteroarene as well as energetic molecules with complex molecular structures and multifunctional groups are difficult, which needs special software. Cao and coworkers [20] have used only some simple energetic compounds in training and test sets. Thus, both QSPR models may have some uncertainty and difficulty for complex molecular structures.

Group additivity methods are suitable methods for estimation of thermochemical properties of organic compounds. For different classes of organic compounds, Sagadeev and coworkers [21,22] have introduced some group contributions in several works to calculate the heats of combustion. Although Sagadeev and coauthors method [21,22] for predicting heats of combustion is very straight-

forward and simple for the calculation based on group contribution, their method can be used only for certain types of nitroaromatic and nitroaliphatic compounds.

Experimental determination of heats of combustion of a new compound is too time-consuming because a pure material and a complete reproducible combustion cannot be easily obtained. Moreover, predicting various properties such as heat of combustion of a notional energetic material is valuable before expending resources. The purpose of this work is to introduce a reliable simple method for predicting the heat of combustion of CHNO energetic compounds. It will be shown that this method can be easily used for important classes of energetic compounds including polynitro arene, polynitro heteroarene, acyclic and cyclic nitramine, nitrate

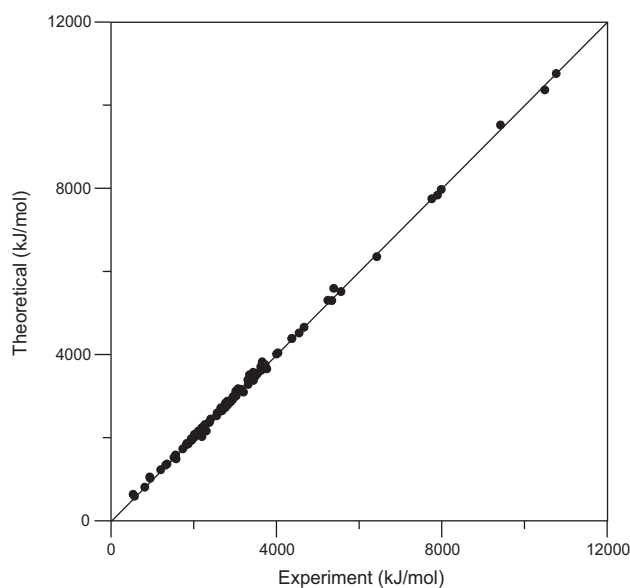


Fig. 1. Calculated gross heats of combustion versus experimental data for different 121 energetic compounds given in Table 1. The solid lines represent exact agreement between predictions and experiment. Filled circles denote calculated results of new method.

Table 2

Comparison of the predicted net heats of combustion of energetic compounds (kJ/mol) by two models of Cao and coworkers [20], multilinear regression (MLR) and artificial neural network (ANN) technique, and the new method with the experimental data.

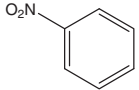
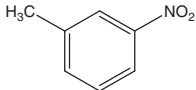
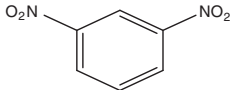
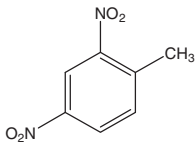
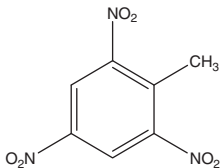
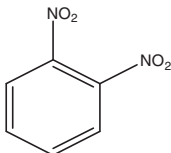
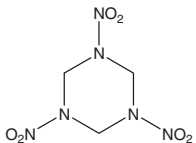
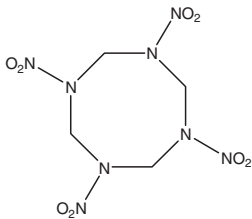
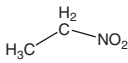
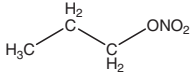
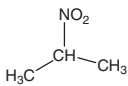
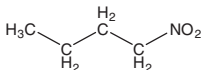
No.	Molecular structure	$-\Delta_c H^\theta$						
		DIPPR 801 [28]	Predicted (MLR)	Dev	Predicted (ANN)	Dev	Predicted (New)	Dev
1		2978.2	3086	-108	3159	-180	2921	58
2		3569.6	3624	-54	3632	-62	3514	55
3		2813.5	3181	-368	3094	-281	2805	9
4		3416	3448	-32	3487	-71	3398	18
5		3295.9	3140	156	3221	75	3282	13
6		2843	2933	-90	3104	-261	2805	38
7		1970	2003	-33	2736	-766	2019	-49
8		2640	1995	645	2398	242	2693	-53
9		1250	1327	-77	1371	-121	1247	3
10		1859	1789	70	1809	50	1841	18
11		1846	1885	-39	1962	-116	1841	5
12		2469.7	2307	163	2315	155	2435	35

Table 2 (Continued)

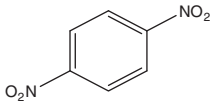
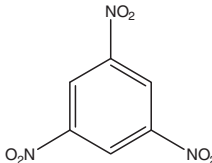
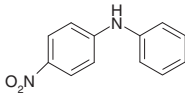
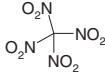


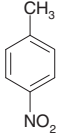
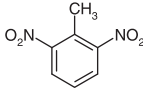
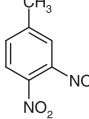
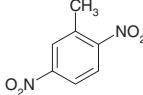
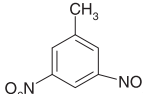

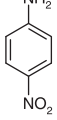


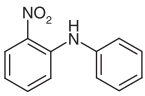
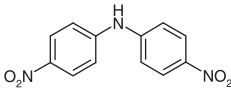
No.	Molecular structure	$-\Delta_c H^\theta$						
		DIPPR 801 [28]	Predicted (MLR)	Dev	Predicted (ANN)	Dev	Predicted (New)	Dev
13		2806.2	3007	-201	3031	-225	2805	2
14		2686.7	2752	-65	2840	-153	2689	-2
15		6022	6281	-259	6173	-151	5977	45
16		643.2	974	-331	1073	-430	653	-10
17		431.8	627	-195	665	-233	305	126
18		3591.4	3600	-8	3609	-17	3514	77
19		3553	3639	-86	3645	-92	3514	39
20		3429	3441	-12	3475	-46	3398	31
21		3466	3427	39	3554	-88	3398	68
22		3446	3462	-16	3448	-2	3398	48
23		3437	3461	-24	3500	-63	3398	39
24		3060	3313	-253	3249	-189	3116	-56
25		3050	3176	-126	3098	-48	3116	-66
25		3060	3309	-249	3213	-153	3116	-56
27		3440	3718	-278	3681	-241	3447	-7

Table 2 (Continued)

No.	Molecular structure	$-\Delta_c H^\theta$						
		DIPPR 801 [28]	Predicted (MLR)	Dev	Predicted (ANN)	Dev	Predicted (New)	Dev
28		6120	6201	-81	6109	11	5977	143
29		5985	6126	-141	5916	69	5861	124
rms deviation (kJ/mol)				199		218		58

ester and nitroaliphatic compounds. The predicted results will be compared to experimental data of mentioned compounds that may have complex molecular structures, where the measured values were available. For some high energy molecules, the reliability of the predicted results will be compared with group additivity method [21,22] and reported results based on atom-type electrotopological state indices [20].

2. Improvement of new model


The study of various energetic compounds including polynitro arene, polynitro heteroarene, acyclic and cyclic nitramine, nitrate ester and nitroaliphatic compounds has shown that a suitable model can be introduced to predict the heat of combustion of CHNO energetic materials. It was found that elemental compositions as well as the presence of some specific polar groups and molecular fragments are important parameters in the new model. Thus, we can write the effects of these parameters for an energetic compound with general formula $C_{a_1}H_{a_2}N_{a_3}O_{a_4}$ in three different terms as follows:

$$-\Delta_c H^\theta = \sum_{i=1}^4 a_i h_i - h_5 \text{ Dec(polar groups)} + h_6 \text{ Inc(molecular fragments)} \quad (1)$$

where $-\Delta_c H^\theta$ is the gross heat of combustion (kJ/mol), h_i is the contribution of the individual atoms and two additional correcting terms. Dec(polar groups) and Inc(molecular fragments) are correcting terms that show the presence of some specific polar groups and molecular fragments in decreasing and increasing the value of heat of combustion on the basis of elemental composition, respectively. The presence of some specific polar groups may affect the predicted values of the condensed phase heat of formation of different classes of energetic compounds because high intermolecular attractions [23]. Meanwhile, it was found that the existence of some molecular fragments may have opposite effects and adjustment of $\sum_{i=1}^4 a_i h_i$ is necessary. The reported gross heat of combustion of 121 of different compounds with various classes including polynitro arene, polynitro heteroarene, acyclic and cyclic nitramine, nitrate ester and nitroaliphatic compounds were collected and are listed in Table 1. Statistical analyses (multiple regressions [24]) of these 121 compounds give the following correlation:

$$-\Delta_c H^\theta \text{ (kJ/mol)} = 418.3a_1 + 109.7a_2 + 107.5a_3 + 67.88a_4 - 237.2 \text{ Dec(polar groups)} + 89.42 \text{ Inc(molecular fragments)} \quad (2)$$

The values of Dec(polar groups) and Inc(molecular fragments) can be specified according to the following situations:

- Predicting Dec(polar groups): The attachment of some specific polar groups such as $-\text{OH}$ to nitroaromatic compounds may decrease enthalpy of formation of energetic compounds [23]. For the existence of one of three functional groups $-\text{OH}$, $-\text{COOH}$ and $-\text{N}-\text{C}(=\text{O})-$ or more than one $-\text{NH}_x$ attached to nitroaromatic ring such as 1,3-diamino-2,4,6-trinitrobenzene (DATB), the value of Dec(polar groups) equals 1.0 that can enhance molecular interactions in this situation.
- Predicting Inc(molecular fragments): It was indicated that the attachment of $-\text{N}=\text{N}-$ to nitroaromatic compound such as 4,4'-dinitroazofurazan can increase the condensed phase enthalpy of formation [23], which can enhance the value of $-\Delta_c H^\theta$. The value of Inc(molecular fragments) in this case or the existence of molecular fragment  in polynitro heteroarenes, e.g., benzotrifuroxane, is equal to 2.0. For mononitro benzene without the presence of polar groups of part (a), Inc(molecular fragments) is also 0.8.

The coefficient of multiple determination (R^2) and the root mean square (rms) deviation mainly reflect the goodness of fit of the models, which are 0.999 and 60 kJ/mol, respectively, for Eq. (2) on the basis of data given in Table 1. The values of Dec(polar groups) and Inc(molecular fragments) are equal to zero if the conditions to assign different values are not met. Fig. 1 provides the comparison between measured data and predictions of new method.

To illustrate the estimation of $-\Delta_c H^\theta$ using Eq. (2) on the calculated values given in Table 1, three typical examples for the compounds with complex molecular structures are presented below:

- Compound 28: $a_1 = 6$, $a_2 = 6$, $a_3 = 4$, $a_4 = 13$, Dec(polar groups) = 0 and Inc(molecular fragments) = 0.
- Compound 97: $a_1 = 17$, $a_2 = 7$, $a_3 = 11$, $a_4 = 16$, Dec(polar groups) = 1.0 and Inc(molecular fragments) = 0.0.
- Compound 103: $a_1 = 6$, $a_2 = 0$, $a_3 = 12$, $a_4 = 9$, Dec(polar groups) = 0 and Inc(molecular fragments) = 2.0.

3. Comparison of new correlation with two new methods

Group contribution and QSPR are two new methods, which can be used to compare the reliability of new correlation. Cao and coworkers [20] calculated the net heat of combustion for several simple nitroaliphatic and carbocyclic nitroaromatic compounds. Table 2 shows the comparison between the predicted results of new correlation and QSPR based on the atom-type electrotopological state (E-state) indices and artificial neural network (ANN) technique. As seen in Table 2, the rms deviations from experiment of the new method, multilinear regression (MLR) and artificial neural network (ANN) employed in modeling of Cao and coworkers [20] are 58, 199 and 218 kJ/mol, respectively. Only five compounds of Table 2 were used in the test set by Cao et al. [20]. Fig. 2 pro-

Table 3
Comparison of the predicted gross heats of combustion (kJ/mol) of energetic compounds by Sagadeev and coauthors method [22] and the new method with the experimental data.

No.	Molecular structure	$-\Delta_c H^\theta$ (Pred)				
		Exp	Predicted (Sagadeev)	Dev	Predicted (New)	Dev
1		4386 [22]	4386	0	4377	8
2		5008 [22]	5025	-17	5015	-7
3		2902 [22]	2910	-8	2892	10
4		2746 [22]	2731	15	2755	-9
5		2322 [22]	2303	19	2382	-60
6		4077 [25]	4028	49	4030	47
7		5554 [27]	5508	46	5487	67
8		3088 [22]	3089	-1	3102	-14
9		3734 [22]	3734	0	3740	-6
10		4379 [22]	4386	-7	4377	2

Table 3 (Continued)

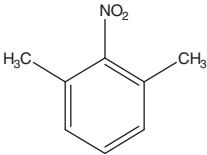
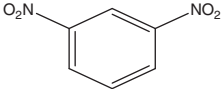
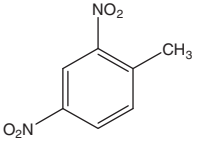
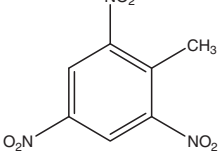
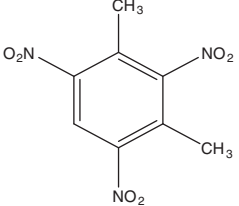
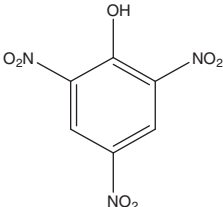
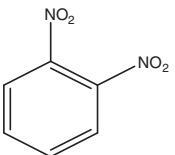
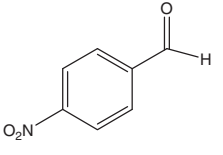
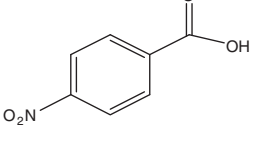
No.	Molecular structure	$-\Delta_c H^\theta$ (Pred)				
		Exp	Predicted (Sagadeev)	Dev	Predicted (New)	Dev
11		4384 [22]	4379	5	4377	7
12		2910 [22]	2910	0	2892	18
13		3551 [22]	3555	-4	3530	21
14		3389 [22] 3395 [27]	3376	13 19	3392	-3 3
15		4044 [22]	4021	23	4030	14
16		2560 [22] 2570 [25]	2517	43 53	2517	43 53
17		2931 [25]	2910	21	2892	39
18		3318 [25]	3343	-25	3381	-63
19		3042 [25]	3050	-8	3076	-34

Table 3 (Continued)

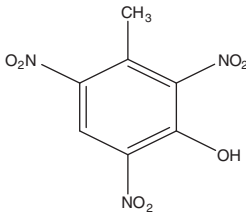
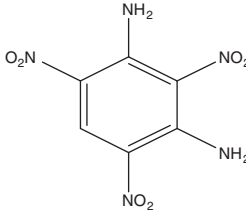
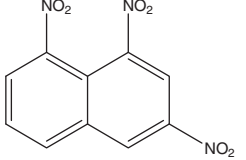
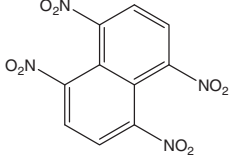
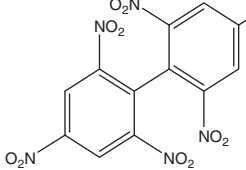
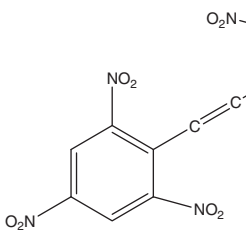
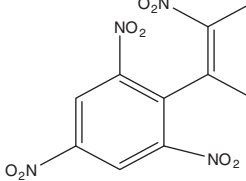
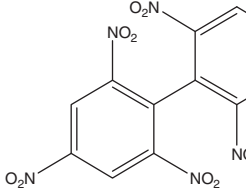
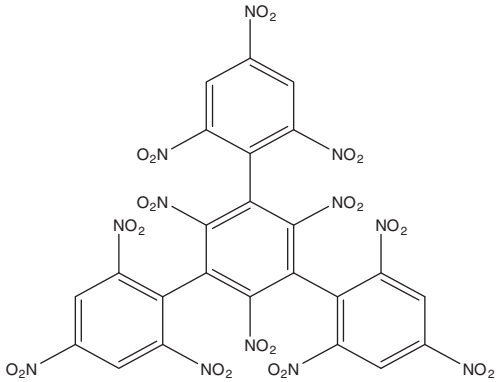
No.	Molecular structure	$-\Delta_c H^\theta$ (Pred)				
		Exp	Predicted (Sagadeev)	Dev	Predicted (New)	Dev
20		3213 [25]	3162	51	3087	126
21		2974 [27]	3047	-73	2952	22
22		4676 [25]	4640	36	4647	29
23		4556 [27]	4461	95	4509	47
24		5350 [27]	5192	158	5290	60
25		6438 [27]	6339	99	6346	92
26		7996 [27]	7833	163	7963	33
27		7905 [27] 7930 [25]	7654	251 276	7825	81 105

Table 3 (Continued)

No.	Molecular structure	$-\Delta_c H^\theta$ (Pred)				
		Exp	Predicted (Sagadeev)	Dev	Predicted (New)	Dev
28		10,504 [27]	10,115	389	10360	144
	rms deviation (kJ/mol)			111		55

vides a visual comparison between experiment and the predictions. Although simple molecules were used in this QSPR method, the predicted results of Eq. (2) for the net heat of combustion are relatively good.

Table 3 compares the predicted results of gross heat of combustion of the new method with group additivity method of Sagadeev and coauthors [21,22]. As indicated in Table 3, the rms deviation from experiment of the new and Sagadeev et al. [21,22] methods are 55 and 111 kJ/mol, respectively. Of twenty-eight compounds given in Table 3, fourteen compounds were used in deriving the values of corresponding group contributions by Sagadeev and coworkers [22]. A visual comparison of the predictions of the new and Sagadeev et al. [21,22] methods with the experimental values is shown in Fig. 3. The method of Sagadeev and coworkers [21,22] cannot be used for some classes of energetic compounds because group contributions of a number of some functional groups and molecular fragments have not been specified. Thus, the method

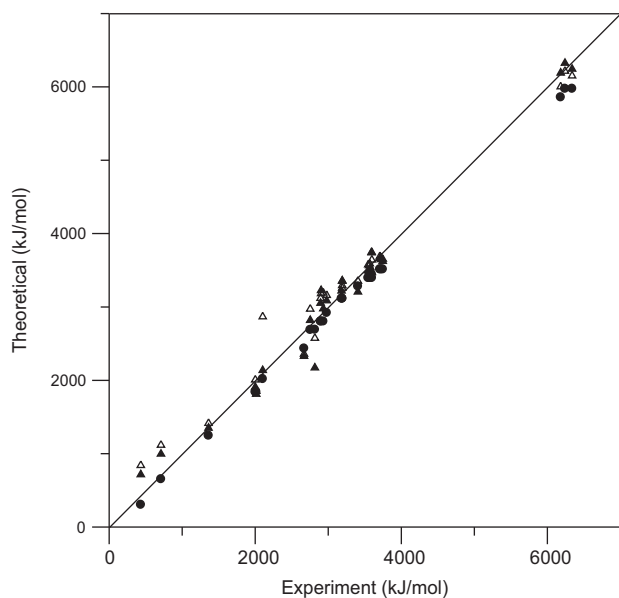


Fig. 2. Calculated net heats of combustion versus experimental data for different 29 energetic compounds given in Table 2. The solid lines represent exact agreement between predictions and experiment. Filled circles denote calculated results of new method. Filled and hollow triangles denote the calculated results by two models of Cao and coworkers [20], i.e., multilinear regression (MLR) and artificial neural network (ANN) technique, respectively.

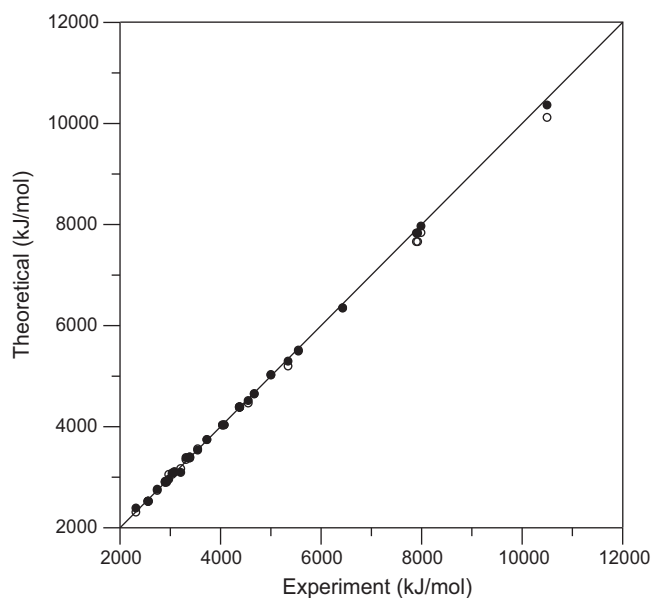


Fig. 3. Calculated gross heats of combustion versus experimental data for different 28 energetic compounds given in Table 3. The solid lines represent exact agreement between predictions and experiment. Filled and hollow circles denote the calculated results by the new and Sagadeev et al. methods [22], respectively.

of Sagadeev and coauthors [21,22] cannot be calculated for many energetic compounds in Table 1, which include polynitro heteroarenes, acyclic and cyclic nitramines and nitrate esters. The last fifteen compounds in Table 2 do not include in Table 1, which confirms the reliability of application of Eq. (2) for further energetic compounds. According to Tables 2 and 3, the rms deviation of the present method is lower than both methods of Cao et al. [20] and Sagadeev and coworkers [21,22]. The latest reported experimental values of the NIST Chemistry Web Book [25] were taken for comparison in Tables 2 and 3.

4. Conclusions

A reliable simple relationship has been introduced for simple predicting the gross and net heats of combustion of important classes of CHNO energetic compounds including polynitro arene, polynitro heteroarene, acyclic and cyclic nitramine, nitrate ester and nitroaliphatic compounds. The new model is based on some

specific polar groups and molecular fragments. The predicted heats of combustion by new method give good results with respect to the model of Cao et al. [20] as well as the method of Sagadeev and coworkers [21,22]. Thus, the method presented here gives the simplest and easiest method for predicting the heats of combustion of the compounds containing energetic nitro, nitrate and nitramine groups.

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