Prediction of the condensed phase heat of formation of energetic compounds

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ABSTRACT

A new reliable simple model is presented for estimating the condensed phase heat of formation of important classes of energetic compounds including polynitro arene, polynitro heteroarene, acyclic and cyclic nitramine, nitrate ester and nitroaliphatic compounds. For CHNO energetic compounds, elemental compositions as well as increasing and decreasing energy content parameters are used in the new method. The novel correlation is tested for 192 organic compounds containing complex molecular structures with at least one nitro, nitramine or nitrate energetic functional groups. This work improves the predictive ability of previous empirical correlations for a wide range of energetic compounds. For those energetic compounds where group additivity method can be applied and outputs of quantum mechanical computations were available, it is shown that the root mean square (rms) deviation of the new method is lower.

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1. Introduction

The condensed phase heat of formation of an energetic compound can be used to investigate its characteristics and thermochemical stability. It enters into the calculation of explosive and propellant properties such as detonation pressure, detonation pressure, detonation temperature, heat of detonation and specific impulse through computer codes or empirical methods [1–3].

Quantum mechanical methods, quantitative structure–property relationship (QSPR) theory, group additivity methods, empirical procedures on the basis of molecular structures, the heat of combustion are suitable methods for predicting the heat of formation of energetic compounds [2,4,5]. Applications of some of these methods in energetic materials have been reviewed elsewhere [2,5]. The condensed phase heats of formation of solid and liquid energetic compounds at 298.15 K can be obtained by combining the gas phase heats of formation with heats of sublimation and vaporization, respectively. Rice et al. [6,7] have used the 6–31G* basis set [8] and the hybrid B3LYP [9,10] density functional for converting quantum mechanical energies of molecules into gas phase heats of formation. They used surface electrostatic potentials of individual molecules for computation of heats of sublimation and vaporization as recommended by Politzer and co-workers [11,12]. Salmon and Dalmazzone [13] developed a suitable group contribution method that can be applied for large classes of CHNO energetic compounds in the solid state (at 298.15 K). Applications of their method have

some restrictions for complex molecular structures such as the definition of many group additivity values, ring strain corrections and the non-nearest neighbor interactions. For some classes of energetic compounds, several simple correlations between different structural parameters have also been developed [14–18]. As an example, it was found that heats of detonation on the basis of Kamlet's method [19] can also be used for predicting solid phase heats of formation of some explosives in the range $Q_{corr} > 4602$ kJ/g [14], where Q_{corr} is the corrected heats of detonation on the basis of Kamlet's method [19].

It is important to have a reliable simple method for predicting the condensed phase heat of formation of a wide range of organic energetic compounds that contain at least one of the functional groups including $-NO_2$, $-O-NO_2$ or $N-NO_2$. The purpose of this work is to improve predictive ability of previous models [14–18], which have been used for certain classes of energetic compounds. The reliability of the new method will be tested for important classes of energetic compounds including polynitro arene, polynitro heteroarene, acyclic and cyclic nitramine, nitrate ester and nitroaliphatic compounds. The estimated results of this method will be compared with the calculated values of group additivity method of Salmon and Dalmazzone [13] as well as outputs of complex quantum mechanical method [6,7].

2. Results and discussion

Since the existence of the variety of different molecular interactions in the condensed phase of energetic compounds, predicting the heat of formation may be difficult. A high density energetic material with a high positive heat of formation may be a good

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Table 1
Comparison of the predicted heats of formation (kJ/mol) of the present and Salmon–Dalmazzone (S–D) [13] methods with experimental data for polynitro arene, polynitro heteroarene, acyclic and cyclic nitramines, nitrate esters and nitroaliphatic energetic compounds that have complex and different molecular structures.

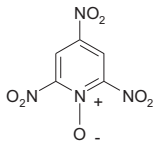| No.	Energetic compound	Experiment	New method	Dev	S–D method	Dev
1	(chemical structure)	−443.4 [27]	(460.8	17.4	(416.8	(26.6
2	(chemical structure)	(422.6 [27]	(460.8	38.3	(416.8	(5.8
3	(chemical structure)	(409.7 [27]	(424.3	14.7	(466.4	56.7
4	(chemical structure)	47.3 [27]	55.7	(8.4	47.8	(0.5
5	(chemical structure)	(15.1 [27]	6.3	(21.3	(9.5	(5.6
6	(chemical structure)	(97.9 [27]	(73.8	(24.1	(110.3	12.4
7	(chemical structure)	296.6 [27]	296.0	0.6	322.6	(26.0
8	(chemical structure)	94.6 [27]	125.6	(31.1	126.0	(31.4
9	(chemical structure)	(114.6 [27]	(135.3	20.6	(114.3	(0.3
10	(chemical structure)	(432.6 [27]	(428.5	(4.1	(455.5	22.9
11	(chemical structure)	(398.7 [27]	(432.7	34.0	(408.1	9.4
12	(chemical structure)	(413.8 [27]	(432.7	18.9	(427.9	14.1

Table 1 (*Continued*)
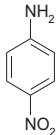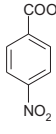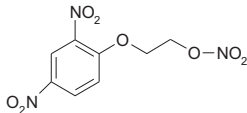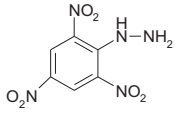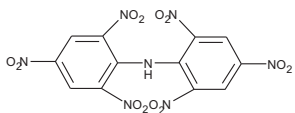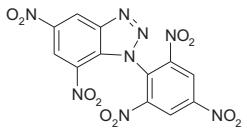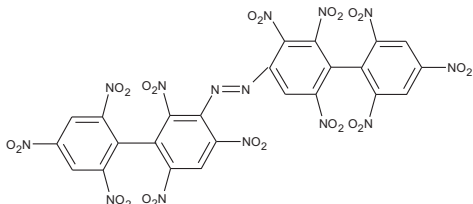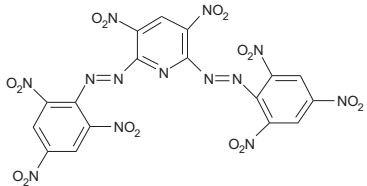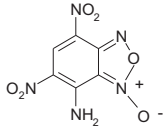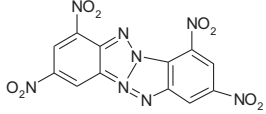
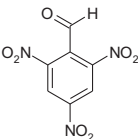| No.	Energetic compound	Experiment	New method	Dev	S–D method	Dev
13	(4-nitroaniline structure)	(45.6 [27]	(60.5	14.9	(22.1	(23.5
14	(4-nitrobenzoic acid structure)	(427.2 [27]	(432.7	5.5	(427.9	0.7
15	(2,4-dinitrophenoxyethyl nitrate structure)	(298.8 [27]	(273.2	(25.6	(287.2	(11.6
16	(2,4,6-trinitrophenylhydrazine structure)	36.5 [27]	0.8	35.7	15.9	20.6
17	(hexanitrodiphenylamine structure)	44.6 [27]	28.0	16.6	(84.8	129.4
18	(benzotriazole picryl structure)	300.0 [27]	330.7	(30.7	297.4	2.6
19	(azo-bis dipicryl structure)	480.3 [27]	478.8	1.6	494.2	(13.9
20	(2,4,6-trinitropyridine N-oxide structure)	98.6 [28]	78.8	19.8	(18.5	117.1
21	(bis(picrylazo)dinitropyridine structure)	617.1 [27]	664.7	(47.5	649.9	(32.8
22	(amino-nitrobenzofurazan N-oxide structure)	86.3 [27]	153.3	(67.0	116.6	(30.3
23	(tetranitrobenzotriazole structure)	461.1 [27]	458.4	2.6	315.4	145.7

Table 1 (*Continued*)
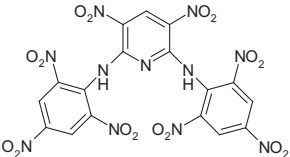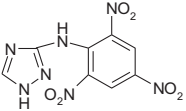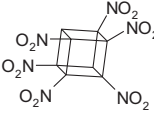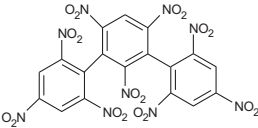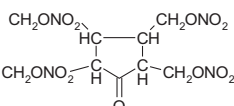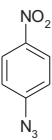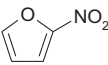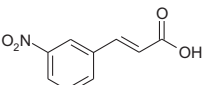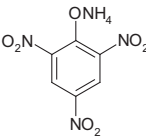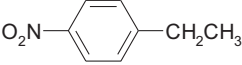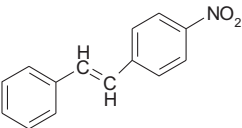
No.	Energetic compound	Experiment	New method	Dev	S–D method	Dev
24		80.3 [27]	83.6	(3.2	(24.7	105.0
25		151.5 [27]	175.6	(24.2	152.5	(1.0
26		200.0 [27]	186.8	13.2		
27		132.2 [27]	129.8	2.4	125.4	6.8
28		(675.8 [28]	(665.2	(10.6	(672.8	(3.0
29		308.7 [27]	309.4	(0.7	203.1	105.6
30	$C(NO_2)_3CN$	174 [27]	135.2	38.8	174.1	(0.1
31		(104 [27]	(88.3	(15.7	(113.8	9.8
32		(370.3 [27]	(363.0	(7.3	(333.6	(36.7
33		(132.8 [27]	(168.5	35.7	(245.3	112.5
34		(386.4 [28]	(418.9	32.5		
35		(55.3 [27]	(48.1	(7.3	(47.1	(8.2
36		102.7 [27]	66.9	35.8	115.9	(13.2
37	$CH_3CH_2CH(NO_2)_2$	(163.2 [27]	(179.0	15.9		
38	$O_2NCH_2CH_2NO_2$	(178.7 [27]	(163.9	(14.8		
39	$O_2NCH_2CH_2CH_2NO_2$	(207.1 [27]	(210.5	3.4		
40	$HOCH_2C(NO_2)(CH_2OH)CH_2OH$	(742.2 [27]	(741.3	(0.9	(776.3	34.1
41	$HOCH_2C(CH_3)_2NO_2$	(410.2 [27]	(400.4	(9.9	(393.9	(16.3

Table 1 (*Continued*)
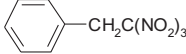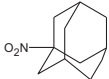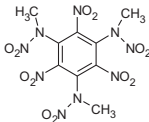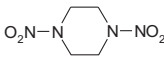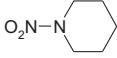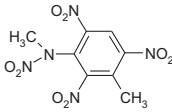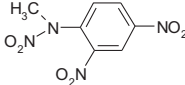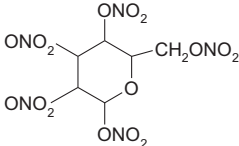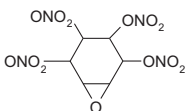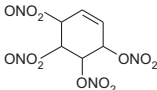
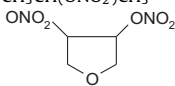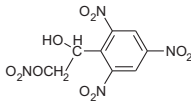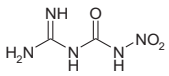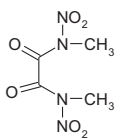| No.	Energetic compound	Experiment	New method	Dev	S–D method	Dev
42	$C(NO_2)_3CH_2OH$	(261.1 [27]	(246.2	(14.9	(232.9	(28.2
43	$CH_3CH_2C(CH_2OH)_2NO_2$	(601.2 [27]	(617.5	16.3	(614.9	13.7
44	$(HOCH_2)_2C(NO_2)(CH_3)$	(570.5 [27]	(570.8	0.3	(585.1	14.6
45	$C(NO_2)_3CH_2OCH_2CH_2C(NO_2)_3$	(402.1 [27]	(437.4	35.3	(397	(5.1
46	$C(NO_2)_3CH_2CH_2C(=O)OCH_2C(NO_2)_3$	(496.2 [27]	(447.7	(48.5	(530.3	34.1
47	$O_2NCH_2CH_2OH$	(350.6 [27]	(307.1	(43.6	(321.5	(29.1
48	$(CH_3)_2C(NO_2)_2$	(192.5 [27]	(179.0	(13.4	(200.6	8.1
49	$O_2NCH_2CH_2CH_2CH_3$	(215.5 [27]	(245.0	29.6		
50	—CH₂C(NO₂)₃ (benzyl)	(18.4 [27]	(39.7	21.3	17.1	(35.5
51	O_2N— (adamantyl)	(254.3 [27]	(272.8	18.5		
52	H₃C, NO₂, CH₃, O₂N·N, N·NO₂, O₂N, NO₂, O₂N·N·CH₃ (substituted ring)	118.0 [27]	85.0	33.0	115.2	2.8
53	O_2N-N N$-NO_2$ (piperazine)	(53.1 [27]	(19.9	(33.3	(52.2	(0.9
54	O_2N-N (piperidine)	(92.9 [27]	(123.6	30.8	(123.7	30.8
55	$CH_3CH_2N(NO_2)CH_2CH_3$	(105.9 [27]	(124.5	18.6	(109.5	3.6
56	$(CH_3)_2NNO_2$	(71.1 [27]	(31.2	(40.0	(10.2	(60.9
57	$CH_3N(NO_2)_2$	1.7 [27]	19.7	(18.0		
58	O₂N, H₃C·N, NO₂, O₂N, O₂N, CH₃ (ring)	10.5 [27]	17.4	(7.0	(55.1	65.6
59	H₃C·N, O₂N, NO₂, O₂N (ring)	16.2 [27]	59.9	(43.7	25.3	(9.1
60	$CH_3CH_2CH_2CH_2N(NO_2)CH_2CH_2ONO_2$	(192.5 [27]	(245.9	53.5	(258.9	66.4
61	$CH_3CH_2N(NO_2)CH_2CH_2ONO_2$	(164.0 [27]	(152.6	(11.4	(229.1	65.1
62	$O_2NOCH_2CH_2N(NO_2)CH_2CH_2ONO_2$	(257.4 [27]	(212.3	(45.1	(289.1	31.7
63	$CH_3CH_2CH_2CH_2CH_2N(NO_2)CH_2CH_2ONO$	(206.7 [27]	(292.6	85.9	(288.7	82.0
64	$CH_3CH_2CH_2N(NO_2)CH_2CH_2ONO_2$	(174.1 [27]	(199.3	25.2	(229.1	55.0
65	ONO₂, ONO₂, CH₂ONO₂, ONO₂, ONO₂ (pyranose ring)	(826.3 [27]	(810.7	(15.7	(840.5	14.2
66	ONO₂, ONO₂, ONO₂, ONO₂, O (epoxide ring)	(444.3 [27]	(471.9	27.6	(444.2	(0.1
67	$O_2NOCH_2CH(OH)CH_2ONO_2$	(477.0 [27]	(477.2	0.3	(476.6	(0.4
68	$HOCH_2CH(OH)CH_2ONO_2$	(577.0 [27]	(588.0	11.1	(578.0	1.0
69	$O_2NOCH_2CH(ONO_2)CH_2CH_2ONO_2$	(414.2 [27]	(413.1	(1.2	(405.0	(9.2
70	$O_2NOCH_2CH_2ONO_2$	(232.6 [27]	(260.1	27.5	(254.8	22.2
71	$O_2NOCH_2CH(ONO_2)CH_3$	(297.1 [27]	(306.7	9.7	(285.4	(11.7
72	$(O_2NOCH_2)_3CCH_3$	(450.2 [27]	(459.7	9.5	(434.5	(15.7
73	$O_2NOCH_2CH_2CH_2CH_2ONO_2$	(274.1 [27]	(353.4	79.3	(314.4	40.3
74	$(O_2NOCH_2)_3CCH_2CH_3$	(479.9 [27]	(506.4	26.5	(464.3	(15.6
75	$CH_3CH(ONO_2)CH_2CH(ONO_2)CH_3$	(385.8 [27]	(400.1	14.3	(345.8	(40.0
76	$(O_2NOCH_2)_2C(NO_2)CH_2CH_3$	(367.4 [27]	(395.9	28.5	(384.9	17.5
77	ONO₂, ONO₂, ONO₂, ONO₂ (cyclohexene ring)	(387.9 [27]	(408.1	20.2	(355.1	(32.8
78	$CH_3C(=O)ONO_2$	(331.0 [27]	(334.6	3.6		
79	$(O_2NOCH_2)_3CCH_2OCH_2C(CH_2ONO_2)_3$	(979.5 [27]	(989.1	9.6	(975.3	(4.2

Table 1 (*Continued*)

No.	Energetic compound	Experiment	New method	Dev	S–D method	Dev
80	$O_2NOCH_2CH_2OCH_2CH_2OCH_2CH_2ONO_2$	(656.9 [27]	(681.0	24.1	(617.8	(39.1
81	$O_2NOCH_2CH_2OCH_2CH_2ONO_2$	(451.0 [27]	(470.6	19.5	(436.3	(14.7
82	$HOCH_2CH(ONO_2)CH_2OH$	(567.8 [27]	(588.0	20.3	(578.0	10.2
83	$HOCH_2CH(ONO_2)CH_2ONO_2$	(472.4 [27]	(477.2	4.9	(476.6	4.2
84	$O_2NOCH_2CH(ONO_2)CH(ONO_2)CH(ONO_2)CH(ONO_2)CH_2ONO_2$	(708.8 [27]	(685.3	(23.4	(736.4	27.6
85	$CH_3CH(ONO_2)CH_3$	(229.7 [27]	(247.1	17.4		
86		(386.0 [27]	(434.2	48.2		
87	$(O_2NOCH_2)_2C(NO_2)CH_3$	(374.0 [27]	(349.2	(24.8	(382.3	8.3
88		(287.7 [27]	(322.3	34.6	(398.3	110.6
89		(302.5 [27]	(299.5	(3.0	(313.3	10.8
90		(305.3 [28]	(335.7	30.4	(302.6	(2.7
	rms deviation			27.8		44.1

candidate of high performance material but its sensitivity can be increased. The heat of formation of an energetic compound is a measure of its energy content that should be considered in designing new energetic compounds. The study of a wide range of different classes of energetic compounds including polynitro arene, polynitro heteroarene, acyclic and cyclic nitramine, nitrate ester and nitroaliphatic compounds has shown that a suitable general model can be introduced to predict their condensed phase heat of formation. For certain nitroalkanes, Chen et al. [20] have shown that the elemental composition can be used to correlate the calculated gas phase heat of formation by semi-empirical molecular orbital methods AM1 and PM3 to the condensed phase heat of formation. Furthermore, previous studies [15–18] have confirmed that elemental composition as well as the other structural parameters can influence the predicted values of the condensed phase heat of formation for some classes of energetic compounds. Due to the presence of high intermolecular interactions, the effect of specific polar groups such as –COOH, –OH, >C=O and –NH$_x$ may be important for increasing thermodynamic stability of energetic compounds. The contributions of polar groups in decreasing of energy content of energetic compounds may be additive [17,18]. Meanwhile, it was found that the contributions of –NO$_2$, –ONO$_2$ and –NNO$_2$ groups may consider constant and in most cases can have opposite effects. The reported condensed phase heat of 90 of different $C_{a_1}H_{a_2}N_{a_3}O_{a_4}$ compounds were collected and listed in Table 1. The optimized correlation using statistical analyses (multiple regressions [21]) of these compounds give the following equation:

$$\Delta_f H^\theta(c) = \Delta_f H^\theta_{EC} + 105.0 \Delta_f H^\theta_{IEC} - 106.6 \Delta_f H^\theta_{DEC} \quad (1)$$

where $\Delta_f H^\theta$ is the condensed phase heat of formation; $\Delta_f H^\theta_{EC} = 32.33a_1 - 39.49a_2 + 92.41a_3 - 63.85a_4$; $\Delta_f H^\theta_{EC}$ is the predicted energy content on the basis of elemental composition; $\Delta_f H^\theta_{IEC}$ and $\Delta_f H^\theta_{DEC}$ are increasing and decreasing energy content parameters, respectively, which can be specified by the contribution of polar groups and some specific molecular fragments. The coefficients 105.0 and −106.6 in Eq. (1) show the relative contributions of $\Delta_f H^\theta_{IEC}$ and $\Delta_f H^\theta_{DEC}$ with respect to $\Delta_f H^\theta_{EC}$. The values of

$\Delta_f H^\theta_{IEC}$ and $\Delta_f H^\theta_{DEC}$ in Eq. (1) are specified in the following situations.

2.1. Prediction of $\Delta_f H^\theta_{DEC}$

Some specific polar groups may contribute to $\Delta_f H^\theta_{DEC}$ through increasing thermodynamic stability of desired energetic compounds. Their contributions can be classified as follows:

(i) *Hydroxyl group* – Two different values 1.4 and 1.0 are contributed to $\Delta_f H^\theta_{DEC}$ for energetic compounds containing –OH group in forms Ar–OH and R–OH, respectively. As an example, $\Delta_f H^\theta_{DEC} = 2 \times 1.4 = 2.8$ for 2,4,6-trinitrobenzene-1,3-diol.

(ii) *Amino (–NH$_x$) groups* – For the existence of mentioned groups, the value contributed to $\Delta_f H^\theta_{DEC}$ is equal to 0.7 (e.g. $\Delta_f H^\theta_{DEC} = 3 \times 0.7 = 2.1$ for 2,4,6-trinitrobenzene-1,3,5-triamine). The presence of –NH$_2$, >NH (or –NH–NH$_2$) in energetic compounds not only may increase thermodynamic stability but also can decrease their sensitivities to specific stimuli, e.g. impact [22,23], electric spark [24] and shock [25], with the goal to design and manufacture less sensitive energetic compounds.

(iii) *Acyclic and cyclic ether functional groups* – The contributions of acyclic and cyclic ether functional groups (except three-membered ring) to $\Delta_f H^\theta_{DEC}$ are 0.5 and 0.9, respectively. As an example, $\Delta_f H^\theta_{DEC} = 1 \times 0.5 = 0.5$ for 2-methoxy-1,3,5-trinitrobenzene.

(iv) *The existence of the other specific polar groups* – For the presence of –COOH (or –ONH$_4$, –COCO– and –NH–CO–), –N–CO–N–, –COO– (or acyclic –CO–), –CO–H, cyclic –CO– and –NH–NO$_2$, the contributions of these groups to $\Delta_f H^\theta_{DEC}$ are 2.8, 2.4, 1.4, 1.0, 0.5 and 0.3, respectively. As an example, $\Delta_f H^\theta_{DEC} = 1 \times 2.8 = 2.8$ for 3,5-dinitrobenzoic acid.

(v) *The number of nitrogen heteroatoms in six-member ring* – For nitroaromatics containing more than one six-member aromatic rings, the contribution of the number of nitrogen heteroatoms in six-membered ring is 0.33. As an example, $\Delta_f H^\theta_{DEC} = 3 \times 0.33 = 0.99$ for 2,4,6-tris(2,4,6-trinitrophenyl)-1,3,5-triazine.

2.2. Prediction of $\Delta_f H^\theta_{IEC}$

The presence of some specific molecular fragments and the attachment of nitro and nitrate groups to non-aromatic carbon as well as cyclic and acyclic nitramines contribute to $\Delta_f H^\theta_{IEC}$, which can be described as follows:

(i) *Cyclic and acyclic nitramine functional groups* – The values of $\Delta_f H^\theta_{IEC}$ are 0.5 and 0.8 for the acyclic and cyclic functional groups, respectively. As an example, $\Delta_f H^\theta_{IEC} = 0.5$ for 1,3,5-trinitro-1,3,5-triazinane.

(ii) *R–NO$_2$ (or R–ONO$_2$) and Ar–N$_3$* – For the attachment of –NO$_2$ or –ONO$_2$ groups to non-aromatic carbon and –N$_3$ group to aromatic ring, the value of $\Delta_f H^\theta_{IEC}$ is 0.3 (e.g. $\Delta_f H^\theta_{IEC} = 0.3$ for 1,1-dinitropropane). There are some exceptions for this case: (a) for the presence –C(NO$_2$)$_3$, $\Delta_f H^\theta_{IEC} = 0.8$ (e.g. $\Delta_f H^\theta_{DEC} = 1.0$ and $\Delta_f H^\theta_{IEC} = 0.8$ for 2,2,2-trinitroethanol); (b) for linear mono-nitroalkanes ($a_1 \geq 4$), $\Delta_f H^\theta_{IEC} = 0.6$ (e.g. $\Delta_f H^\theta_{IEC} = 0.6$ for 1-nitrobutane); (c) for hydrogen free nitroalkanes, $\Delta_f H^\theta_{DEC} = 2.2$ (e.g. $\Delta_f H^\theta_{IEC} = 2.2$ for tetranitromethane); (d) for symmetric linear di-nitroalkanes, $\Delta_f H^\theta_{DEC} = 0.0$ (e.g. $\Delta_f H^\theta_{DEC} = 0.0$ for 1,2-dinitroethane).

(iii) *Molecular fragments –N=N– and* $\overset{N-O^-}{\underset{+}{\diagup\!\diagup}}$ – For molecular fragments $\overset{N-O^-}{\underset{+}{\diagup\!\diagup}}$ and –N=N–, the contributions to $\Delta_f H^\theta_{IEC}$ are 0.7 and 0.8, respectively. As an example, $\Delta_f H^\theta_{IEC} = 3 \times 0.7 = 2.1$ for benzenetrifuroxan.

(iv) *The number of carbocyclic aromatic rings (n_{Ar})* – For those energetic compounds containing only carbocyclic aromatic rings, the contribution to $\Delta_f H^\theta_{IEC}$ is $(n_{Ar} - 1) \times 0.3$. The value of $\Delta_f H^\theta_{IEC}$ is $(2 - 1) \times 0.3 = 0.3$ for 2,2′,4,4′,6,6′-hexanitrobiphenyl as representative example.

(v) *Attachment of alkyl groups to aromatic ring* – The values of $\Delta_f H^\theta_{IEC}$ are 0.2 and 0.8 for the attachment of methyl and higher carbon alkyl groups (or –CH=CH–) to aromatic ring, respectively. As an example, $\Delta_f H^\theta_{IEC} = 0.2$ for 1-methyl-2,4-dinitrobenzene. If $n_{Ar} > 1$, it is not necessary to include previous condition, i.e. (iv).

(vi) *Nitro groups attached to non-aromatic four-membered ring* – For the attachment of –NO$_2$ groups to non-aromatic four-membered ring, the contribution to $\Delta_f H^\theta_{IEC}$ is 0.45 (e.g. $\Delta_f H^\theta_{IEC} = 8 \times 0.45$ for octanitrocubane).

The coefficient of multiple determination (R^2) deviation mainly reflects the goodness of fit of the model, which is 0.983, for Eq. (1) on the basis of data given in Table 1. The values of $\Delta_f H^\theta_{IEC}$ and $\Delta_f H^\theta_{DEC}$ are equal to zero if the conditions to assign different values are not met.

3. Comparison of the new correlation with outputs of quantum mechanical and group additivity methods

Quantum mechanical computations of Rice et al. [6,7] as well as group contribution procedure of Salmon and Dalmazzone (S–D) [13] are two new and suitable methods, which can be used to compare the reliability of the new correlation. Table 1 shows the comparison between the predicted results of the new correlation and the S–D method. As seen in Table 1, the root mean square (rms) deviations from experiment of the new and the S–D methods are 27.8 and 44.1 kJ/mol, respectively, which confirm the reliability of the present work. A visual comparison of the predicted results of Eq. (1) and the S–D method with the experimental values is shown in Fig. 1. For some energetic compounds, Rice et al. [6,7] have com-
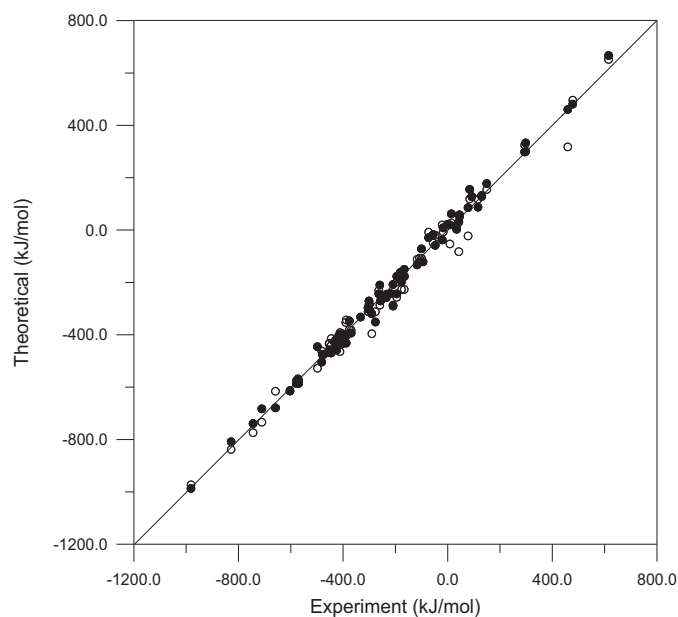

Fig. 1. Calculated condensed phase heats of formation versus experimental data for different 90 energetic compounds given in Table 1. The solid lines represent exact agreement between predictions and experiment. Filled and hollow circles denote the calculated results of the new and the S–D [13] methods, respectively.

puted the condensed phase heat of formation. Table 2 compares the predicted results of the new method with reported outputs of Rice et al. [6,7] as well as group additivity of the S–D method [13]. As indicated in Table 2, the rms deviations from experiment of the new, quantum mechanical and the S–D methods are 18.9, 43.9 and 29.7 kJ/mol, respectively. A visual comparison of the predictions of three mentioned methods with experiment is also given in Fig. 2. As seen in Tables 1 and 2, group additivity of the S–D method [22] has some restrictions and cannot be used in some classes of energetic compounds for the following reasons:
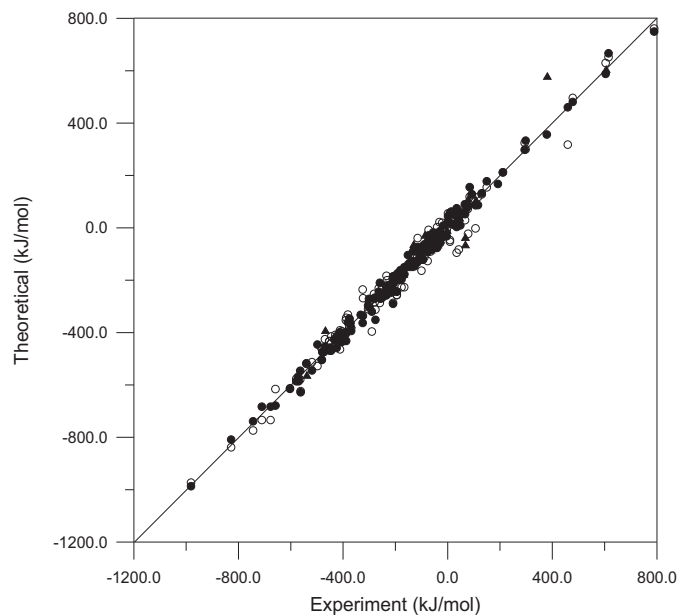

Fig. 2. Calculated condensed phase heats of formation versus experimental data for different 49 energetic compounds given in Table 2. The solid lines represent exact agreement between predictions and experiment. Filled and hollow circles denote calculated results of the new and the S–D [13] methods. Filled triangles denote the calculated quantum mechanical outputs by Rice et al. [6,7].

Table 2
Comparison of the predicted condensed heats of formation (kJ/mol) from the new, quantum mechanical (QM) [6,7] and Salmon–Dalmazzone (S–D) [13] methods with experimental data.
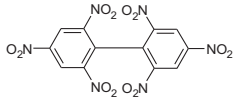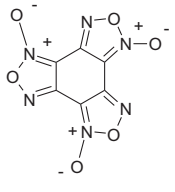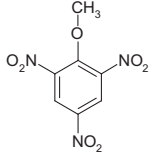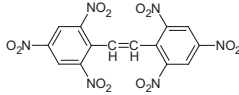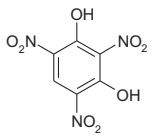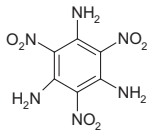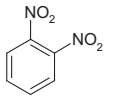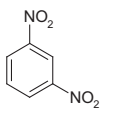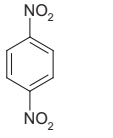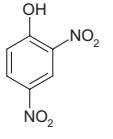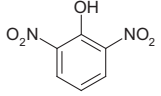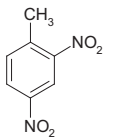
No.	Name	Experiment	New method	Dev	QM	Dev	S–D method	Dev
1		68.2 [27]	49.7	18.5	(67.8	136.0	27.3	40.9
2		606.3 [27]	585.8	20.4	602.1	4.2	627.6	(21.3
3		(187.2 [27]	(194.2	7.0	(184.1	(3.1	(174.2	(13.0
4		67.8 [27]	87.9	(20.1	(39.7	107.5	78.2	(10.4
5		(467.5 [27]	(456.6	(10.9	(395.0	(72.6	(427.9	(39.6
6		(74.7 [27]	(95.6	20.9	(87.0	12.3	(128.8	54.1
7		(1.7 [27]	(34.6	32.9	(12.6	10.9	(10.0	8.3
8		(27.2 [27]	(34.6	7.4	(50.2	23.0	(42.8	15.6
9		(38.5 [27]	(34.6	(3.9	(38.5	0.0	(36.8	(1.7
10		(235.5 [27]	(247.7	12.2	(228.9	(6.7	(219.9	(15.6
11		(209.6 [27]	(247.7	38.1	(200.0	(9.6	(219.9	10.3
12		(66.4 [27]	(60.2	(6.2	(84.9	18.5	(69.6	3.2

Table 2 (*Continued*)
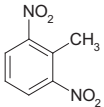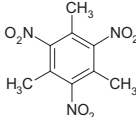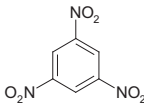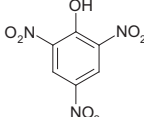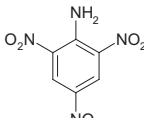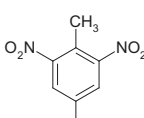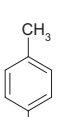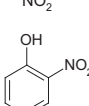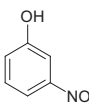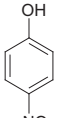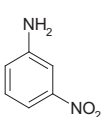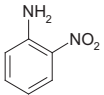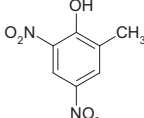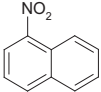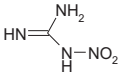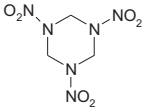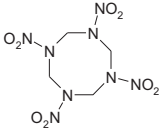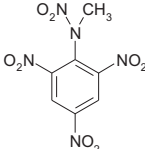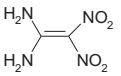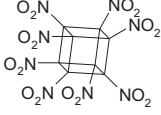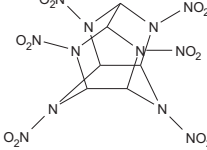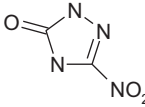
No.	Name	Experiment	New method	Dev	QM	Dev	S–D method	Dev
13	2-methyl-1,3-dinitrobenzene (structure)	(55.2 [27]	(60.2	5.0	(64.0	8.8	(61.9	6.7
14	trimethyltrinitrobenzene (structure)	(124.5 [27]	(149.3	24.9	(135.6	11.1	(130.8	6.3
15	1,3,5-trinitrobenzene (structure)	(37.2 [27]	(30.4	(6.9	(68.6	31.4	(73.5	36.3
16	2,4,6-trinitrophenol (structure)	(217.9 [27]	(243.5	25.6	(226.8	8.9	(250.7	32.8
17	2,4,6-trinitroaniline (structure)	(72.8 [27]	(52.1	(20.7	(89.1	16.3	(92.0	19.2
18	2,4,6-trinitrotoluene (structure)	(63.2 [27]	(56.0	(7.1	(87.4	24.3	(92.6	29.4
19	4-nitrotoluene (structure)	(48.2 [27]	(64.4	16.2	(66.5	18.3	(46.5	(1.7
20	2-nitrophenol (structure)	(204.6 [27]	(188.0	(16.6	(190.0	(14.6	(189.2	(15.4
21	3-nitrophenol (structure)	(205.7 [27]	(188.0	(17.6	(193.3	(12.4	(209.0	3.3
22	4-nitrophenol (structure)	(207.1 [27]	(188.0	(19.1	(208.4	1.3	(209.0	1.9
23	3-nitroaniline (structure)	(36.4 [27]	(60.5	24.1	(26.4	(10.0	(22.1	(14.3
24	2-nitroaniline (structure)	(26.4 [27]	(60.5	34.1	(32.2	5.9	(26.2	(0.2
25	2-methyl-4,6-dinitrophenol (structure)	(279.1 [27]	(273.4	(5.7	(270.3	(8.8	(254.4	(24.7

Table 2 (*Continued*)

No.	Name	Experiment	New method	Dev	QM	Dev	S–D method	Dev
26		45.7 [27]	43.1	2.7	34.3	11.4	43.0	2.7
27	CH_3NO_2	(112.5 [27]	(89.9	(22.6	(114.6	2.1		
28	$CH_2(NO_2)_2$	(104.9 [27]	(85.7	(19.2	(96.2	(8.7		
29	$CH(NO_2)_3$	(68.0 [27]	(81.5	13.6	(45.2	(22.8		
30	$C(NO_2)_4$	38.5 [27]	58.3	(19.8	38.1	0.4		
31	$CH_3CH_2NO_2$	(143.9 [27]	(136.6	(7.3	(155.2	11.3		
32	$C(NO_2)_3C(NO_2)_3$	108.4 [27]	83.9	24.5	101.7	6.7	(4.1	112.5
33	$CH_3CH_2CH_2NO_2$	(167.4 [27]	(183.2	15.9	(180.3	13.0		
34	$CH_3CH(NO_2)CH_3$	(180.3 [27]	(183.2	2.9	(189.1	8.8		
35	$CH_3CH_2CH_2CH_2NO_2$	(192.6 [27]	(198.4	5.8	(202.9	10.3		
36	$CH_3CH(NO_2)CH_2CH_3$	(207.6 [27]	(198.4	(9.2	(210.9	3.3		
37	$(CH_3)_3C(NO_2)$	(229.7 [27]	(229.9	0.2	(225.1	(4.6	(202.6	(27.1
38	$CH_3CH_2ONO_2$	(190.4 [27]	(200.4	10.0	(203.3	12.9		
39	$CH_2(ONO_2)CH(ONO_2)CH_2ONO_2$	(369.9 [27]	(366.4	(3.5	(370.7	0.8		
40	$CH_3CH_2CH_2ONO_2$	(214.6 [27]	(247.1	32.5	(227.2	12.6		
41	$C(CH_2ONO_2)_4$	(538.5 [27]	(519.4	(19.1	(566.1	27.6	(521.7	(16.8
42		(86.6 [27]	(65.0	(21.6	(31.0	(55.6	(114.2	27.6
43		75.3 [27]	94.3	(19.0	87.0	(11.7	69.4	5.9
44		79.1 [27]	83.9	(4.8	107.1	(28.0	69.5	9.6
45		41.0 [27]	64.1	(23.1	(7.1	48.1	(5.5	46.5
46		(133.9 [29]	(128.4	(5.5	(82.0	(51.9		
47		381.2 [30]	354.3	26.8	575.7	(194.6		
48		377.4 [31]	352.2	25.2	415.1	(37.7		
49		(129.4 [32]	(92.2	(37.3	(66.5	(62.9		
	rms deviation			18.9		43.9		29.7

(i) The S–D method can be used to estimate only the solid state heat of formation of $C_{a_1}H_{a_2}N_{a_3}O_{a_4}$ energetic compounds. However, the S–D method cannot be applied for those energetic compounds that have liquid state at 298.15 K.

(ii) Group contributions of a number of some functional groups for energetic compounds have not been defined in the S–D method. Thus, this method cannot be used to calculate the solid phase heat of formation of some new energetic compounds such as 2,2-dinitroethene-1,1-diamine (FOX-7).

(iii) Cage energetic compounds are important new energetic compounds because they have not only high energy content but also provide high density, which give high energy density com-

Table 3
Comparison of theoretically predicted heats of formation (kJ/mol) of the present and Salmon–Dalmazzone (S–D) [13] methods with experimental data for some further energetic compounds including well-known explosives.
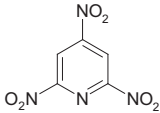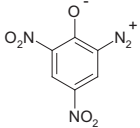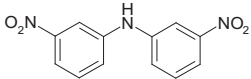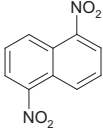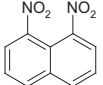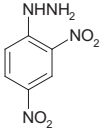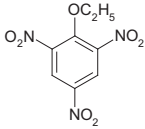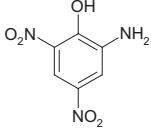
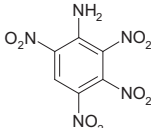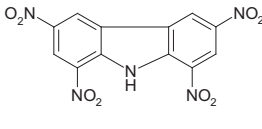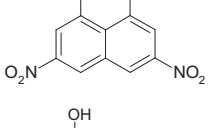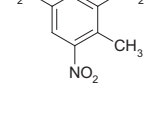| No.	Energetic compound	Experiment	New method	Dev	S–D method	Dev
1	2,4,6-trinitropyridine	78.8 [28]	69.2	9.6	(13	91.8
2	diazonium nitrophenolate	194.0 [28]	165.4	28.6		
3	bis(3-nitrophenyl)amine	22.9 [28]	11.2	11.6	38.0	(15.1
4	1,5-dinitronaphthalene	30.6 [28]	47.3	(16.7	12.2	18.4
5	1,8-dinitronaphthalene	37.6 [28]	47.3	(9.6	60.8	(23.2
6	2,4-dinitrophenylhydrazine	50.0 [28]	7.3	42.7	46.7	3.3
7	ethoxy trinitrobenzene	(200.8 [28]	(240.8	40.1	(196.7	(4.1
8	amino dinitrophenol	(248.1 [28]	(269.4	21.3	(229.9	(18.2
9	amino tetranitrobenzene	(48.9 [28]	(47.9	(1.0	(63.9	15.0
10	tetranitrocarbazole	18.9 [28]	67.1	(48.2	3.2	15.7
11	tetranitronaphthalene	10.8 [28]	55.7	(44.8	(49.2	60.0
12	trinitromethylphenol	(252.1 [28]	(269.2	17.0	(269.8	17.7

Table 3 (*Continued*)
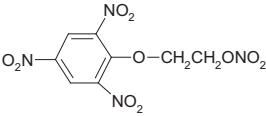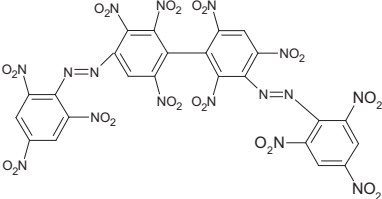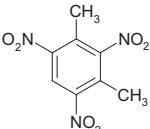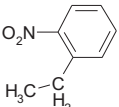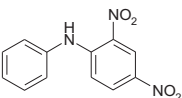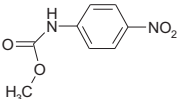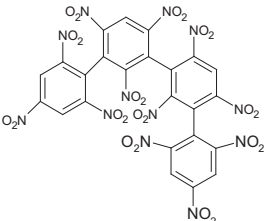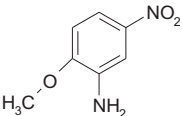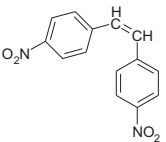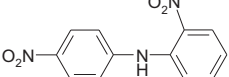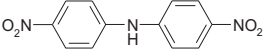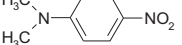
No.	Energetic compound	Experiment	New method	Dev	S–D method	Dev
13	(structure: trinitrophenyl-O-CH₂CH₂ONO₂)	(277.3 [28]	(269.0	(8.3	(286.6	9.3
14	(structure: bis-azo trinitrophenyl compound)	791.6 [27]	747.6	44.0	759.3	32.3
15	(structure: dimethyl tetranitrobenzene)	(102.5 [28]	(102.7	0.1	(111.7	9.2
16	(structure: nitro-ethyl-benzene)	(48.7 [27]	(48.1	(0.6	(39.4	(9.3
17	(structure: N-phenyl-2,4-dinitroaniline)	22.5 [27]	11.2	11.3	38.0	(15.5
18	(structure: methyl carbamate nitrophenyl)	(427.9 [27]	(426.4	(1.5	(411.3	(16.6
19	(structure: terphenyl with many NO₂ groups)	213.0 [27]	209.9	3.0	209.8	3.2
20	(structure: methoxy-amino-nitrobenzene)	(232.0 [27]	(224.3	(7.7	(185.5	(46.5
21	(structure: bis(nitrophenyl)ethylene)	74.1 [27]	71.1	3.0	85.1	(11.0
22	$C(NO_2)_3CH_2CH_2CN$	3.4 [27]	41.9	(38.5	52.8	(49.4
23	(structure: bis(2-nitrophenyl)amine)	22.9 [28]	11.2	11.7	38	(15.1
24	(structure: nitrophenyl-nitrophenylamine)	22.9 [28]	11.2	11.7	38	(15.1
25	(structure: bis(4-nitrophenyl)amine)	22.9 [28]	11.2	11.7	18.2	4.7
26	(structure: N,N-dimethyl-4-nitroaniline)	(38.5 [27]	(79.2	40.7	0.1	(38.6

Table 3 (*Continued*)
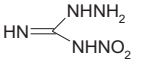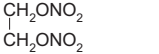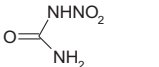
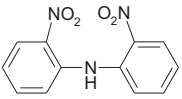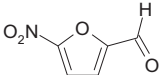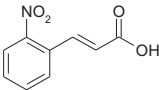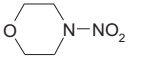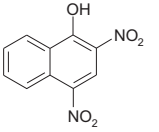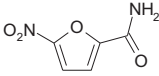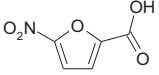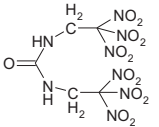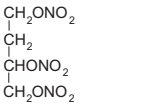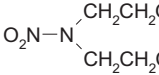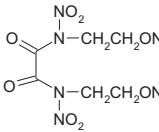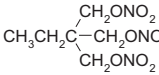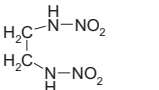| No.	Energetic compound	Experiment	New method	Dev	S–D method	Dev
27	(structure: 5-nitrofuran-2-carbaldehyde)	(227.0 [27]	(226.4	(0.6	(227.3	0.3
28	(structure: 2-nitrocinnamic acid)	(379.9 [27]	(363.0	(16.9	(333.6	(46.3
29	(structure: N-nitromorpholine)	(213.0 [27]	(236.8	23.8	(215.8	2.8
30	(structure: 2,4-dinitronaphthalen-1-ol)	(172.0 [27]	(165.9	(6.1	(164.9	(7.1
31	(structure: 5-nitrofuran-2-carboxamide)	(323.0 [27]	(365.5	42.5	(237.8	(85.2
32	(structure: 5-nitrofuran-2-carboxylic acid)	(517.1 [27]	(546.9	29.8	(515.3	(1.8
33	$C(NO_2)_3CH_3$	(113.0 [27]	(75.7	(37.3	(41.6	(71.4
34	$CH_3N(NO_2)CH_2N(NO_2)CH_3$	(29.8 [27]	(20.7	(9.1	19.7	(49.5
35	(structure)	(321.7 [28]	(338.0	16.3	(270.9	(50.8
36	(structure)	(405.9 [28]	(413.1	7.2	(405	(0.9
37	(structure)	(192.3 [28]	(245.9	53.6	(258.9	66.6
38	(structure)	(561.7 [28]	(548.3	(13.4	(581.6	19.9
39	(structure)	(479.5 [28]	(506.4	26.9	(463.3	(16.2
40	(structure)	(103.7 [28]	(122.0	18.3	(103.8	0.1
41	(structure)	(675.5 [28]	(685.3	9.8	(736.4	60.9
42	(structure)	22.1 [28]	(12.1	34.1	4.1	18.0
43	(structure)	(242.7 [28]	(260.1	17.4	(254.8	12.1
44	(structure)	(282.3 [28]	(288.4	6.1	(226.6	(55.7

Table 3 (*Continued*)

No.	Energetic compound	Experiment	New method	Dev	S–D method	Dev
45	HOCH$_2$C(CH$_2$ONO$_2$)(CH$_2$ONO$_2$)CH$_2$ONO$_2$	(560.4 [28]	(630.2	69.8	(625.7	65.3
46	[-CH$_2$CH(ONO$_2$)-]$_n$	(102.6 [28]	(121.5	18.9		
47	(H$_3$C)(H$_3$C)CH–ONO$_2$	(229.3 [28]	(247.1	17.8		
48	O$_2$N–N–C(H$_2$)–C(H$_2$)(NO$_2$)–NO$_2$	36.4 [28]	72.6	(36.2	(97.0	133.4
49	O$_2$N–N, N–NO$_2$ triazinone with NO$_2$	(41.8 [27]	(77.9	36.1	(57.9	16.1
50	O$_2$N–C(NO$_2$)(NO$_2$)–N(CH$_2$)–CH$_2$CH$_2$ONO$_2$	(98.3 [27]	(87.5	(10.8	(165.8	67.5
51	O$_2$NOCH$_2$CH$_2$–N(NO$_2$)–CH$_3$	(149.8 [27]	(106.0	(43.8	(143.3	(6.5
52	nitrated sugar structure	(1364.0 [27]	(1363.4	(0.6	(1364.0	0.0
53	O$_2$N–C(NO$_2$)(H$_2$)–N(NO$_2$)–C(H$_2$)(NO$_2$)–NO$_2$	(28.0 [27]	(15.3	(12.7	(42.5	14.5
54	O$_2$NOCH$_2$–C(CH$_3$)(NO$_2$)–CH$_2$–ONO$_2$	(374.0 [27]	(349.2	(24.8	(379.6	5.6
	rms deviation		26.4			40.1

pounds. Salmon and Dalmazzone [13] have not determined ring–strain corrections for ε-hexanitrohexaisowurtzitane and β-hexanitrohexaisowurtzitane. However, application of the S–D method without ring–strain corrections gives large deviation with respect to experimental data. For example, the predicted solid heat of formation of octanitrocubane by the S–D method is −539.4 kJ/mol with large deviation 920.6 kJ/mol.
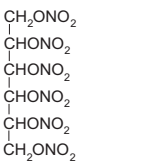
Quantum mechanical method of Rice et al. [6,7] requires high speed computer and complex Gaussian suite of quantum chemistry codes [26]. Furthermore, it takes high computer times for large energetic molecules and, as seen in Table 2, its rms deviation is higher than both the new and the S–D methods.

To examine the application of the present method for some further energetic compound with complex molecular structures and different molecular fragments, the calculated values for 54 energetic compounds are also given in Table 3. A comparison of new model with the S–D method for some energetic compounds in the solid phase is also given in Table 3. As shown in Table 3, the rms deviation of this new method is lower than that of the S–D method. Fig. 3 provides a visual comparison between experiment and the predictions of present work and the S–D method. As indicated in Tables 1–3, the present work provides much better results than Rice et al. computations [6,7] and the S–D method [13].

Since there are different values for the condensed phase heats of formation reported from different sources in Tables 1–3, the latest reported values of the NIST Chemistry Web Book [27] were taken to compare the above mentioned method with the experimental data. For example, −32.1, −68.8 and −77.95 kJ/mol are three reported values for trinitromethane or 44.56 and 76.27 kJ/mol are two different reported experimental data for bis(2,4,6-trinitrophenyl)amine [23]. However, due to large experimental errors in determination of the condensed phase heat of formation of energetic compounds, the predictive results of present model may be useful with respect to two of the best available methods, i.e. quantum mechanical based method and group additivity procedure.
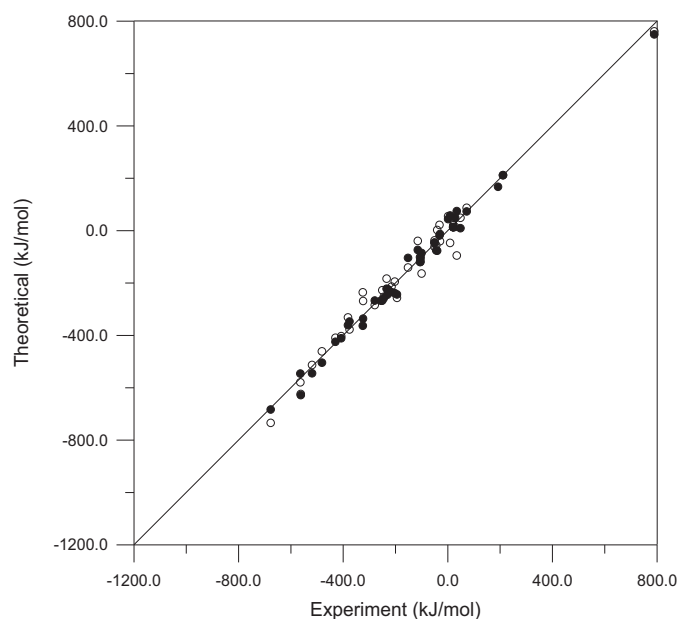
Fig. 3. Calculated condensed phase heats of formation versus experimental data for different 54 energetic compounds given in Table 3. The solid lines represent exact agreement between predictions and experiment. Filled and hollow circles denote the calculated results of the new and the S–D [13] methods, respectively.

4. Conclusions

A novel reliable simple correlation has been introduced to predict the condensed phase heats of formation in polynitro arene, polynitro heteroarene, acyclic and cyclic nitramines, nitrate esters and nitroaliphatic energetic compounds. Elemental composition and two increasing and decreasing energy content parameters are important factors in the new model, which uses the contribution of polar groups and some specific molecular fragments. As shown in Tables 1–3, the predictions for 192 molecules containing energetic bonds –NO_2, –ONO_2, –NNO_2 with this new method provides reliable results with respect to both quantum mechanical [7,8] and the S–D [9] methods.

Acknowledgements

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