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Validation of improved simple method for prediction of activation energy of the thermal decomposition of energetic compounds

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Abstract This study presents a new simple model for predicting activation energy of the thermolysis of various classes of energetic compounds. The new model can help to elucidate the cause of thermal stability and, therefore, shelf life of some energetic compounds. The methodology assumes that activation energy of an energetic compound with general formula $C_aH_bN_cO_d$ can be expressed as a function of optimized elemental composition as well as the contribution of specific molecular structural parameters. The new correlation has the root mean square and the average deviations of 9.8 and 7.4 kJ mol^{-1}, respectively, for 86 energetic compounds with different molecular structures. The proposed new method is also tested for 20 energetic compounds, which have complex molecular structures, e.g. 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane, 2,4,6-tris(2,4,6-Trinitrophenyl)-1,3,5-triazine and 1-(2,4,6-Trinitrophenyl)-5,7-dinitrobenzotriazole.

Keywords Energetic compound · Thermal decomposition · Activation energy · Shelf life

Introduction

Energetic materials can be classified into three categories, i.e. propellants, explosives and pyrotechnics [1–4]. Propellants and pyrotechnics release their energy through relatively slow deflagration processes. Meanwhile, explosives can liberate their energy during fast detonation processes in microsecond timescale [5]. Energetic compounds can be divided into different classes such as nitramines, nitroparaffins, polynitro arenes, polynitro heteroarenes and nitrate compounds.

Quantum mechanical and empirical methods can help the chemists to improve systematic and scientific formulation of appropriate futuristic target molecules having enhanced performance as well as good thermal stability, impact and friction sensitivity. Due to the expenditure connected with the development and synthesis of a new energetic material, different theoretical approaches can be used to determine performance, sensitivity and physicochemical properties of energetic compounds before their synthesis [6–10].

High performance, low sensitivity and good shelf life are three important characteristics of an ideal energetic compound. Especially thermal stability of energetic materials is an important feature in their shelf life and safety aspects [11–13]. Low sensitivity and high thermal stability of energetic compounds are necessary to avoid undesirable decomposition or self-initiation during their handling, storing and the application themselves. Prediction of thermal stability on mentioned compounds is an important starting point to evaluate the stability.

For thermolysis of nitramines, it was found that the homolysis of the N–NO_2 bond is a primary step of the secondary nitramines whereas the homolysis of primary nitramines is a bimolecular autoprotolytic reaction [14]. However, the longest N–N bonds are responsible for homolytic reactivity of nitramines, which may contribute strongly to the intermolecular potential in the crystal state. Moreover, some linear relationships have been introduced for selected classes of nitramines between their activation

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energies of decomposition with ^{15}N NMR chemical shifts of nitrogen atoms of nitramino groups [15], heats of detonation or the electronic charges at nitrogen atoms of the nitramines [16, 17]. The electronic charges at nitrogen atoms of nitramines can be computed on the basis of the Muliken population analysis of the electron densities obtained by ab initio DFT B3LYP/6-31G** method [18]. The values of crystal lattice energies of nitramines do not generally differ from those of polynitroaromatics [19]. For evaluation of the results of non-isothermal differential thermal analysis, the activation energy as the slope in the Kissinger relationship [20] can be used.

The study of thermolysis of energetic compounds can be used for estimation of their thermal stability [21, 22]. The experimental data for thermal reactivity can be obtained by various methods of thermal analysis and gasometry or by a variety of methods based on thermal explosion [19, 20, 23–25]. For example, differential thermal analysis (DTA), differential scanning calorimetry (DSC) and thermogravimetric analysis methods are thermoanalytical methods that are used widely to examine the kinetic parameters of thermolysis of energetic materials. Also the Soviet Manometric Method (SMM) is the isothermal manometric method with a glass-compensating manometer of the Bourdon type to examine the kinetics of thermolysis of energetic materials in vacuum. The data obtained by this method are the basic data on the Arrhenius parameters of non-autocatalyzed thermal decomposition of energetic materials. Moreover, if a relationship such as calibration curve exists between the results of DTA and DSC with the results of SMM, the results of DTA and DSC can be converted to SMM data [26–31]. There is no uniform classification of a large majority of results obtained in various laboratories all over the world because there is a discrepancy in principles and physical conditions of kinetics measurements in the thermolysis of energetic materials.

Zeman [32] have also used the modified Evans–Polanyi–Semenov (E–P–S) equation in the study of the chemical micromechanism governing the initiation of detonation of energetic materials. The original E–P–S equation [33, 34] describes a relationship between the activation energy, E, of the most substitution reactions and corresponding heats of reaction, ΔH. Zeman [32] has substituted ΔH by heat of explosion and E by E_a of the low temperature thermal decomposition, which can lead to the modified E–P–S equation for energetic materials.

Some new correlations have been developed to estimate activation energy of the thermolysis of different classes of energetic compounds separately [35–37], but they cannot be used for variety energetic compounds with different molecular structure. The purpose of this work is to improve a new general correlation for prediction of activation energy of thermolysis of organic energetic materials with general molecular formula $C_aH_bN_cO_d$. How elemental composition and several structural parameters can be used to derive a novel correlation will be shown. When decision is to design new energetic materials, it is necessary to consider contribution of non-additive structural parameters in addition to elemental composition.

Materials and methods

More accurate and reliable data source on the activation energies of the non-autocatalyzed thermal decomposition in the condensed state of energetic compounds is on the basis of SMM [26–31]. Since disagreement in principles and physical conditions prevents a uniform classification of a large majority of results obtained in various laboratories, the existing literature also lacks a more complete survey of the published activation energy of the monomolecular non-autocatalyzed thermal decompositions. Table 1 shows experimental data of various classes of energetic compounds contacting energetic groups $-NNO_2$, $-ONO_2$, $-CNO_2$ or $-NNO$ groups, which can act as active sites for thermal decomposition of energetic compounds. Most data of activation energy of energetic compounds in literature are based on SMM because it can minimize the effects of consecutive reactions of intermediates and products of thermal decomposition both with each other and with the starting energetic material.

Due to the presence of various factors affecting the experimental data of activation energies for different classes of energetic compounds [26], at first it seems difficult to obtain a general correlation to predict E_a for these compounds. Fortunately, the study of the activation energies for thermal decomposition of various explosives has shown that it is possible to derive a general novel correlation for predicting activation energy of energetic materials.

The results show that the important factors can be divided into additive and non-additive structural parameters. Thus, the following equation can be used as a suitable correlation:

$$E_a = 166.36 + 2.85n_C - 21.2n_{OH} + 31.98E^{+}_{non-add} - 44.93E^{-}_{non-add} \quad (1)$$

where E_a is activation energy in kJ mol^{-1}; the parameters n_C and n_{OH} represent the number of carbon atoms and hydroxyl groups, respectively; the functions $E^{+}_{non-add}$ and $E^{-}_{non-add}$ show increasing and decreasing contribution of non-additive structural parameters, respectively. The existence of some molecular moieties in form $E^{+}_{non-add}$ and $E^{-}_{non-add}$ can correct the predicted results on the basis of additive part.

Table 1 Comparison of the predicted activation energy for 86 different types of energetic compounds with experimental data

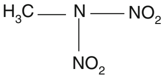
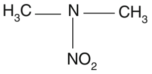
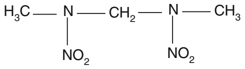
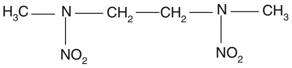
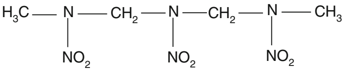
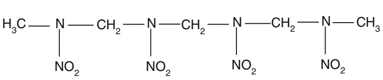
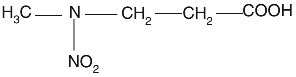
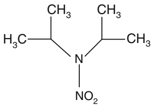
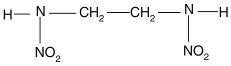
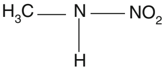
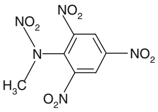
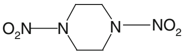
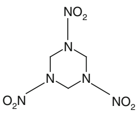
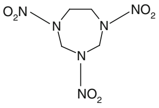
No.	Name	Compound	E_a(exp)/ kJ mol^{-1}	E_a(cal)/ kJ mol^{-1}	Dev
1	1,1-Dinitro-1-azaethane (MDN)	 $H_3C-\underset{NO_2}{N}-NO_2$	168.40 [a]	169.21	–0.8
2	1-Nitro-1-azaethylene (DIGEN)	$H_2C=N-NO_2$	156.00 [a]	169.21	–13.2
3	2-Nitro-2-azapropane (DMNA)	 $H_3C-\underset{NO_2}{N}-CH_3$	166.08 [b]	172.06	–5.9
4	2,4-Dinitro-2,4-diazapentane (OCPX)	 $H_3C-\underset{NO_2}{N}-CH_2-\underset{NO_2}{N}-CH_3$	178.60 [a]	174.91	3.7
5	2,5-Dinitro-2,5-diazahexane (DMEDNA)	 $H_3C-\underset{NO_2}{N}-CH_2-CH_2-\underset{NO_2}{N}-CH_3$	176.10 [a]	177.76	–1.7
6	2,4,6-Trinitro-2,4,6- triazaheptane (ORDX)	 $H_3C-\underset{NO_2}{N}-CH_2-\underset{NO_2}{N}-CH_2-\underset{NO_2}{N}-CH_3$	178.09 [a]	177.76	0.3
7	2,4,6,8-Tetranitro-2,4,6,8-tetraazanonane (OHMX)	 $H_3C-\underset{NO_2}{N}-CH_2-\underset{NO_2}{N}-CH_2-\underset{NO_2}{N}-CH_2-\underset{NO_2}{N}-CH_3$	180.60 [a]	180.61	0.0
8	4-Nitro-4-azavaleric acid (NVA)	 $H_3C-\underset{NO_2}{N}-CH_2-CH_2-COOH$	176.18 [c]	177.76	–1.6
9	Dipropylnitramine (DPN)	$(C_3H_7)_2NNO_2$	201 [d]	183.46	17.5
10	Diisopropylnitramine (DIPN)		178 [d]	183.46	–5.5
11	1,4-Dinitro-1.4-diazabutane (EDNA)	 $H-\underset{NO_2}{N}-CH_2-CH_2-\underset{NO_2}{N}-H$	186.2 [a]	172.06	14.4
12	1-Nitro-1-azaethane (MNA)	 $H_3C-\underset{H}{N}-NO_2$	128.1 [a]	135.51	–7.4
13	1-Methylnitramino-2,4,6- trinitrobenzene (TETRYL)		157.04 [e] 156.9 [a]	152.61	4.4 4.3
14	1,4-Dinitro-1,4- iazacyclohexane (DNDC)		165.79 [f]	177.76	–12.0
15	1,3,5-Trinitro-1,3,5-triazacyclohexane (RDX)		166.83 [g] 167 [a]	174.91	–8.1 –7.9
16	1,3,5-Trinitro-1,3,5- triazacycloheptane (HOMO)		200.8 [a] 207.1 [n]	209.74	–8.9 –2.6

Table 1 continued

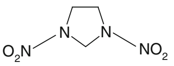
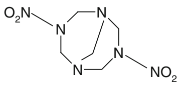
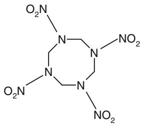
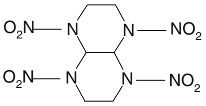
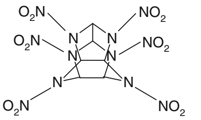
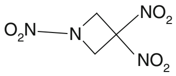
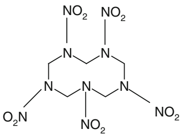
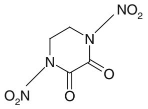
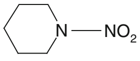
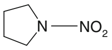
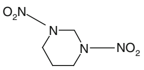
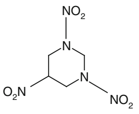
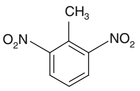
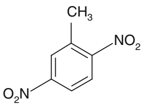
No.	Name	Compound	E_a(exp)/ kJ mol^{-1}	E_a(cal)/ kJ mol^{-1}	Dev
17	1,3-Dinitro-1,3-diazacyclopentane (CPX)		149.4 [f]	156.94	–7.5
18	1,5-Endomethylene-3,7-dinitro-1,3,5-tetraazacyclooctane (DPT)		195.10 [a] 192.30 [h]	180.61	14.5 11.7
19	1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane (HMX)		214.7 [g] 214.60 [i] 209.00 [j]	209.74	4.2 4.1 –7.2
20	1,4,5,8-Tetranitro-1,4,5,8-tetraazadecahydronaphthalene (TNAD)		217.60 [h] 210.00 [k] 209.00 [k]	215.44	2.2 –5.4 –6.4
21	2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (HNIW)		172.26 [l]	183.46	–11.2
22	1,3,3-Trinitroazatidine (TNAZ)		153.5 [m]	156.94	–3.4
23	1,3-Dinitro-1,3-diazacyclobutane (TETROGEN)		153.1 [a]	154.09	–0.1
24	1,3,5,7,9-Pentanitro-1,3,5,7,9-Pentaazacyclodecane (DECAGEN)		213.5 [a] 201.8 [a]	212.59	0.9 –10.8
25	2,5-Dinitro-2,5-diazahexane-3,4-dione (DMNO)		178.8 [a]	177.76	1.0
26	N-nitropiperidine (NPIP)		202 [d]	212.59	–10.6
27	N-nitropyrrolidine (NPyr)		215 [d]	209.74	5.3
28	1,3-Dinitro- 1,3-diazacyclohexane (mDNP)		175 [d]	177.76	–2.8
29	1,3,5-Trinitro-1,3-diazacyclohexane (TNP)		181.1 [n]	177.76	3.3
30	2,6-Dinitrotoluene (2,6-DNT)		198.87 [n]	186.31	12.6
31	3,5-Dinitrotoluene (3,5-DNT)		186.08 [n]	186.31	–0.2

Table 1 continued

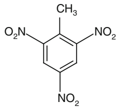
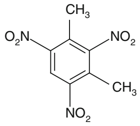
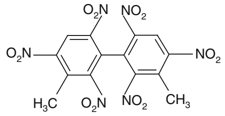
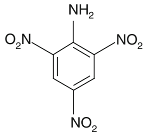
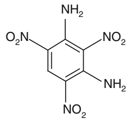
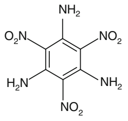
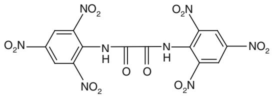
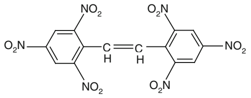
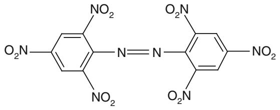
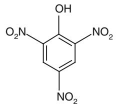
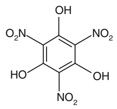
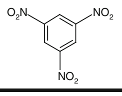
No.	Name	Compound	E_a(exp)/ kJ mol^{-1}	E_a(cal)/ kJ mol^{-1}	Dev
32	2,4,6-Trinitrotoluene (TNT)		144.44[n] 143.30[n]	141.38	3.1 1.9
33	2,4-Dimethyl-1,3,5-trinitrobenzene (TNX)		146.95[n]	144.23	2.7
34	3,3'-Dimethyl-2,2',4,4',6,6'-hexanitro-1,1'-biphenyl (DMHNB)		106.4[n]	116.4	–10.0
35	2,4,6-Trinitroaniline (PAM)		129.79[n]	138.53	–8.7
36	2,4,6-Trinitrobenzene-1,3-diamine (DATB)		196.80[n] 193.72[n]	183.46	13.3 10.3
37	2,4,6-Trinitrobenzene-1,3,5-triamine (TATB)		175.00[n]	183.46	–8.5
38	N,N'- Bis(2,4,6-trinitrophenyl)oxamide (HNO)		215.62[n]	206.26	9.4
39	(E)-2,2',4,4',6,6'-Hexanitrosilbene (HNS)		183.80[n]	206.26	–22.5
40	(E)-Bis(2,4,6-trinitrophenyl) diazene (HNAB)		121.83[n]	110.7	11.1
41	2,4,6-Trinitrophenol (PA)		161.18[n]	162.26	–1.1
42	2,4,6-Trinitrobenzene-1,3,5-triol (TNPg)		114.64[n]	119.86	–5.2
43	1,3,5-Trinitrobenzene (TNB)		180.03[n]	183.46	–3.4

Table 1 continued

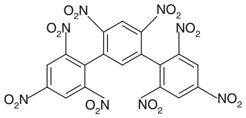
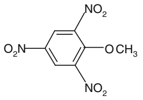
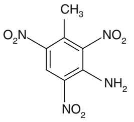
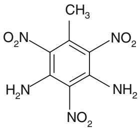
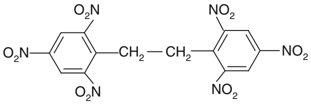
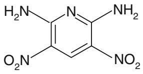
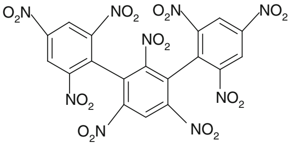
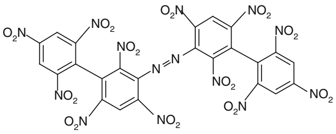
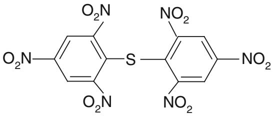
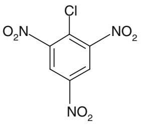
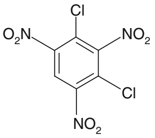
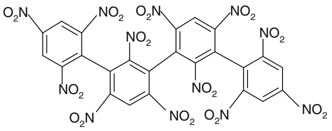
No.	Name	Compound	E_a(exp)/ kJ mol^{-1}	E_a(cal)/ kJ mol^{-1}	Dev
44	2,2',2",4,4',6,6',6"-Octanitro-1,1':3',1"-terphenyl (ONT)		281.58[n]	281.62	0.0
45	2,4,6-Trinitroanisole (TNA)		113.80[n]	118.92	–5.1
46	3-Amino-2,4,6-trinitrotoluene (ATNT)		134[o]	141.38	–7.4
47	3,5-Diamino-2,4,6-trinitrotoluen (DATNT)		137[o]	141.38	–4.4
48	a,b-Bis(2,4,6-Trinitrophenyl)ethane (DPE)		124[n]	116.4	7.6
49	2,6-Diamino-3,5-dinitropyridine (DADNP)		224.5[n]	212.59	11.9
50	2,2´,2",4,4´,4",6,6´,6"-Nonanitro-m-terphenyl (NONA)		236.30[p] 214.11[n]	217.66	18.6 –3.6
51	Azo-bis(2,2',4,4',6,6'-hexanitrobiphenyl) (ABH)		223.56[n]	234.76	–11.2
52	2,2´,4,4´,6,6´-Hexanitrodiphenylsulfide (DIPS)		131.8[n]	133.16	–1.4
53	1-Chloro-2,4,6-trinitrobenzene (CTB)		118.07[n]	116.06	2.0
54	1,3-Dichloro-2,4,6-trinitrobenzene (DCTB)		177.09[n]	183.46	–6.4
55	2,2´,2",4,4´,4",6,6´,6"-Dodecanitro-m-quaterphenyl (DODECA)		217.48[n]	217.66	–0.2

Table 1 continued

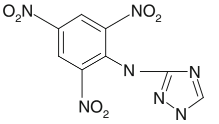
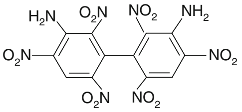
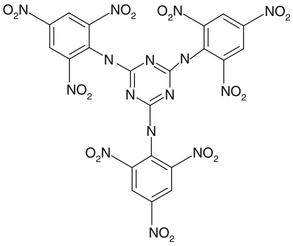
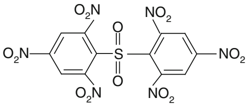
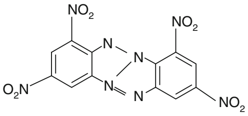
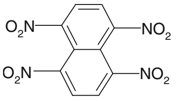
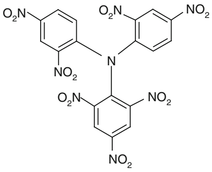
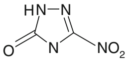
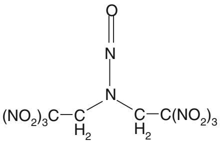
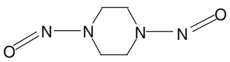
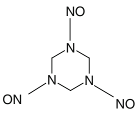
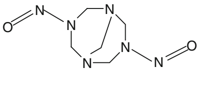
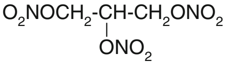
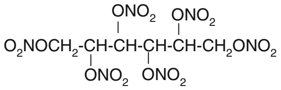
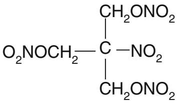
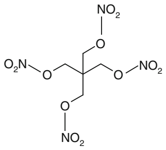
No.	Name	Compound	E_a(exp)/ kJ mol^{-1}	E_a(cal)/ kJ mol^{-1}	Dev
56	3-(2,4,6-Trinitrophenylamino)-1,2,4-triazole (PATO)		134.72 [n]	144.23	–9.5
57	3,3´-Diamino-2,2´,4,4´,6,6´-hexanitrobiphenyl (DIPAM)		190.23 [q]	200.56	–10.3
58	2,4,6-Tris(2,4,6-Trinitrophenylamino)-1,3,5-triazine (TPM)		257.06 [n]	258.19	–1.1
59	2,2',4,4',6,6'-Hexanitrodiphenylsulfone (DIPSO)		106.76 [n]	110.7	–3.9
60	1,3,7,9-Tetranitro-1,3a,4,6a-tetraazapentalene (TACOT-1)		234.3 [n]	232.54	1.8
61	1,4,5,8-Tetranitronaphthalene (TENN)		223.05 [n]	226.84	–3.8
62	N,N-Bis(2,4-dinitrophenyl) -2,4,6-trinitroaniline (NTFA)		187.00 [p]	183.96	3.0
63	5-Nitro-1,2,4-triazol-3-one (NTO)		172 [r]	172.06	–0.1
64	Bis(2,2,2-Trinitroethyl)-N-nitrosamine (BTN)		148.11 [n]	144.06	4.1
65	1,4-Dinitroso-1,4-diazacyclohexane (DNSP)		143.94 [n]	144.06	–0.1
66	1,3,5-Trinitroso-1,3,5-triazcyclohexane (TMTA)		144.35 [n] 146.94 [n]	141.21	3.1 5.7
67	1,5-Endomethylene-3,7-dinitroso-1,3,5,7-tetraazacyclooctane (DNPT)		144.2 [n]	146.91	–2.7
68	Ethylnitrate (EtN)	$CH_3—CH_2NO_3$	167.36 [n]	158.58	8.8

Table 1 continued

No.	Name	Compound	E_a(exp)/ kJ mol^{-1}	E_a(cal)/ kJ mol^{-1}	Dev
69	1,4-Butylene glycol dinitrate (1,4-BGDN)	$O_2NO-CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2-ONO_2$	163.18 [n]	164.28	–1.1
70	Ethylene glycol dinitrate (EGDN)	$O_2NOCH_2CH_2ONO_2$	163.28 [n]	158.58	4.7
71	Glycerol trinitrate (NG)	 $O_2NOCH_2\text{-}\underset{ONO_2}{CH}\text{-}CH_2ONO_2$	163.3 [n]	161.43	1.9
72	Manitol hexanitrate (MHN)	 $O_2NOCH_2\text{-}\underset{ONO_2}{CH}\text{-}\overset{ONO_2}{CH}\text{-}\underset{ONO_2}{CH}\text{-}\overset{ONO_2}{CH}\text{-}CH_2ONO_2$	159.1 [n]	170.0	–10.9
73	Trimethylolnitromethane trinitrate (NIBNG)	 $O_2NOCH_2-\underset{CH_2ONO_2}{\overset{CH_2ONO_2}{C}}-NO_2$	152.3 [n]	164.28	–2.0
74	Pentaerythritol tetranitrate (PETN)		163.17 [n] 175 [s]	167.13	–4.0 7.9
75	Nitromethane (NM)	CH_3NO_2	227.19 [t]	233.17	–6.0
76	Trinitromethane	$CH(NO_2)_3$	177.4 [t]	169.21	8.2
77	Tetranitromethane (TENM)	$C(NO_2)_4$	170.96 [t] 159.83 [t]	169.21	1.8 –9.4
78	Nitroethane	$CH_3CH_2NO_2$	232.4 [v] 253.55 [u]	236.02	–3.6 17.5
79	1,1,1- Trinitronitroethane	$CH_3C\ (NO_2)_3$	180.57 [v]	172.06	8.5
80	Hexonitronitroethane	$C\ (NO_2)_3\ C\ (NO_2)_3$	162.60 [u] 149.79 [t]	172.06	–9.4 –22.3
81	1,1-Dinitropropane	$CH_3CH_2CH(NO_2)_2$	200.83 [t]	206.89	–6.1
82	2,2- Dinitropropane	$CH_3C(NO_2)_2CH_3$	211.09 [u] 198.74 [t]	206.89	4.2 –8.1
83	1,1,1-Trinitropropane	$CH_3CH_2C\ (NO_2)_3$	176.98 [v]	174.91	2.1
84	1,1- Dinitrobutane	$CH_3CH_2\ CH_2CH(NO_2)_2$	201.5 [t]	209.74	–8.2
85	1,1,1-Trinitrobutane	$CH_3CH_2\ CH_2C\ (NO_2)_3$	182.42 [v]	177.76	4.7
86	Dinitromethane (DNM)	$O_2N\text{-}CH_2\text{-}NO_2$	163 [n]	169.21	–6.2
	The rms deviation/ kJ mol^{-1}				9.8
	The average absolute deviation/ kJ mol^{-1}				7.4

[a] Ref [10], [b] Ref [31], [c] Ref [45], [d] Ref [25], [e] Ref [46], [f] Ref [47], [g] Ref [48], [h] Ref [26], [I] Ref [49], [j] Ref [50], [k] Ref [51], [l] Ref [52], [m] Ref [15], [n] Ref [32], [o] Ref [24], [p] Ref [53], [q] Ref [31], [r] Ref [23], [s] Ref [22], [t] Ref [54], [u] Ref [55], [v] Ref [56].

Experimental data from different sources given in Table 1 were used to derive Eq. (1) through multiple linear regression method [38]. Deviations of experimental data from the estimated results on the basis of additive part have been used to find non-additive structural parameters. Since the existence of a variety of different factors influences activation energy, large deviations exist between experimental data for some energetic compounds. Fortunately, R^2 value or the coefficient of determination of Eq. (1) is 0.92. Structural moieties affecting $E^{+}_{\text{non-add}}$ and $E^{-}_{\text{non-add}}$are described in next sections.

Results and discussion

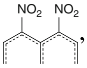
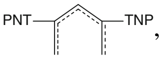
Prediction of $E^{+}_{\text{non-add}}$

The presence of some structural parameters can increase activation energy because they may enhance thermal stability of energetic compound.

(a) *Cyclic nitramines* This condition can be applied for cyclic nitramines belonging to one of the following classes:

  (i) more than six-membered ring and two –NNO_2 groups;
  (ii) more than four-membered ring with only one –NNO_2 group;
  (iii) bicyclic ring with only two –NNO_2 groups per cycle. The value of $E^{+}_{\text{non-add}}$ is 1.0 for these compounds. For cyclic nitramines, this condition is consistent with correlation of activation energy in which their activation energies increase with the size of ring [36].

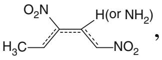
(b) *Nitroalkanes* For nitroalkanes with molecular moieties R–CH_2NO_2 and R–$C(NO_2)_2$–R′, the values of $E^{+}_{\text{non-add}}$ are 2.0 and 1.0, respectively.

(c) *Niroaromatics* Two different situations are considered here: (i) For the presence of amino pyridine derivative, , triazine ring or four adjacent nitrogens in nitroaromatics, the value of $E^{+}_{\text{non-add}}$ is equal to 1.0. (ii) The value of $E^{+}_{\text{non-add}}$ equals 2.0 for the existence of molecular fragment , where TNP is 2,46-trinitrophenyl.

Estimation of $E^{-}_{\text{non-add}}$

(a) *Acyclic nitramines and cyclic nitramines including small ring* For those acyclic nitramines with only one –NNO_2 group in form Ar(or H)–$N(NO_2)CH_3$, the value of $E^{-}_{\text{non-add}}$ is equal to 0.75. The value of $E^{-}_{\text{non-add}}$ equals 0.4 for cyclic nitramines containing less than five membered ring or five membered ring with more than one N–NO_2.

(b) *Niroaromatics* Several types of molecular fragments can be considered in this category:

  (i) For the presence of molecular moieties –O(or S)–R(or Ar), the values of $E^{-}_{\text{non-add}}$ equal 1.5;
  (ii) For the existence of molecular fragment , the value of $E^{-}_{\text{non-add}}$ is equal to the number of this molecular moiety;
  (iii) The values of $E^{-}_{non-add}$ are 1.5, 1.0 and 0.75 for the compound TNP–X where X are –Cl, –NH– and –N<, respectively;
  (iv) For energetic compounds with general formula TNP–Y–TNP where Y are –N=N–, –CH_2–CH_2– and –SO_2–, the value of $E^{-}_{\text{non-add}}$ equals 2.0.

(c) *The presence of nitrate group* For the existence of -ONO_2 group, the value of $E^{-}_{\text{non-add}}$ equals 0.3.

(d) *The existence of nitroso group* The value of $E^{-}_{\text{non-add}}$ is 0.75.

Reliability of the predicted results and the effects of non-additive structural parameters

As seen in Table 1, predicted activation energies for different types of energetic compounds have a root mean square

Table 2 Standardized coefficients and some statistical parameters of Eq. (1)

Variable	Coefficient	Standard error	*P* value	Lower bound (95 %)	Upper bound (95 %)
Intercept	166.3613	1.725572	0.0000	162.9374	169.7852
n_C	2.850439	0.222894	0.0000	2.40817	3.292708
n_{OH}	−21.8517	2.748602	0.0000	−27.3055	−16.3979
$E^{+}_{\text{non-add}}$	31.98026	2.106707	0.0000	27.8001	36.16043
$E^{-}_{\text{non-add}}$	−44.9296	2.105702	0.0000	−49.1077	−40.7514

Table 3 Comparison of the predicted activation energy with experimental data for 20 energetic organic compounds with complex molecular structures

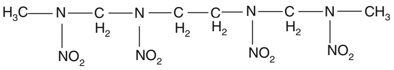
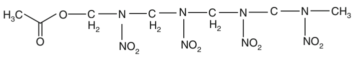
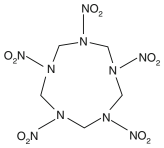
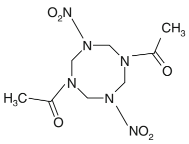
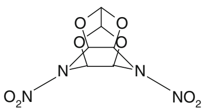
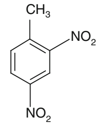
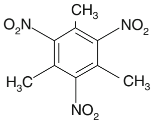
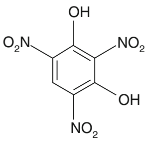
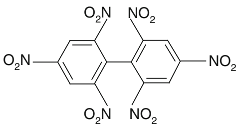
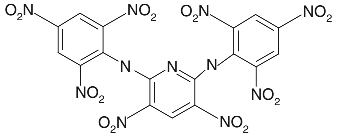
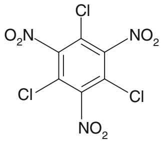
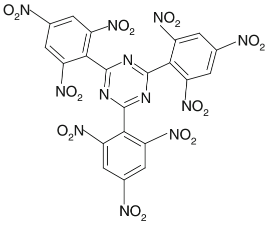
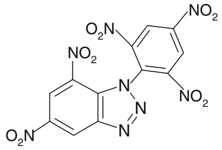
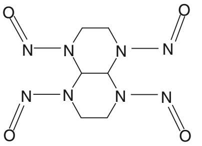
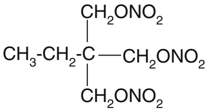
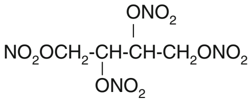
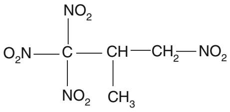
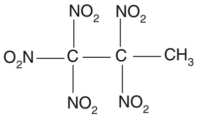
No.	Name	Compound	E_a(exp)/ kJ mol^{-1}	E_a(cal)/ kJ mol^{-1}	Dev
1	2,4,7,9-Tetranitro-2,4,7,9-tetraazadecane (TNADEC)	 $H_3C-\underset{NO_2}{N}-\underset{H_2}{C}-\underset{NO_2}{N}-\underset{H_2}{C}-\underset{H_2}{C}-\underset{NO_2}{N}-\underset{H_2}{C}-\underset{NO_2}{N}-CH_3$	179.00 [a] 183.70 [a]	183.46	–4.5 0.3
2	1,9-Diacetoxy-2,4,6,8-tetranitro-2,4,6,8-tetraazanonane (AcAn)	 $H_3C-\underset{O}{C}-O-\underset{H_2}{C}-\underset{NO_2}{N}-\underset{H_2}{C}-\underset{NO_2}{N}-\underset{H_2}{C}-\underset{NO_2}{N}-C-\underset{NO_2}{N}-CH_3$	199.70 [a] 202.40 [a] 213.00 [a] 214.00 [a]	186.31	13.4 16.1 26.7 27.7
3	Diethylnitramine (DEN)	$(C_2H_5)_2NNO_2$	189 [d]	177.76	11.2
4	1,3,5,7, 9-Pentanitro-1,3,5,7, 9-pentaazacyclodecane (DECAGEN)		201.80 [n] 213.50 [n]	212.59	–10.8 0.9
5	1,5-Diacetyl-3,7-dinitro-1,3,5,7-Tetraazacyclooctane (DADN)		189.1 [n]	189.16	–0.1
6	4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane (TEX)		196.8 [n]	183.46	13.3
7	2,4-Dinitrotoluene (2,4-DNT)		139.56 [n]	141.38	–1.8
8	2,4,6-Trimethyl-1,3,5-trinitrobenzene (TNMs)		185.08 [n]	192.01	–6.9
9	2,4,6-Trinitrobenzene-1,3-diol (TNR)		144.88 [n]	141.06	3.8
10	2,2',4,4',6,6'-Hexanitro-1,1'-biphenyl (HNB)		207.24 [n]	200.56	6.7
11	2,6-Bis(2,4,6-Trinitrophenylamino)-3,5-dinitropyridine (PYX)		213 [n]	214.81	–1.8

Table 3 continued

No.	Name	Compound	E_a(exp)/ kJ mol^{-1}	E_a(cal)/ kJ mol^{-1}	Dev
12	1,3,5-Trichloro-2,4,6-trinitrobenzene (TCTB)		185.77^{n}	183.46	2.3
13	2,4,6-Tris(2,4,6-Trnitrophenyl)-1,3,5-triazine (TPT)		269.45^{n}	258.19	11.3
14	1-(2,4,6-Trinitrophenyl)-5,7-dinitrobenzotriazole (BTX)		214.85^{n}	200.56	14.3
15	1,4,5,8-Tetranitroso-1,4,5,8-tetraazadecahydronaphthalene (TNSAD)		149.15^{n} 150.10^{n}	149.76	–0.6 0.3
16	1,1,1-Trimethylolpropane trinitrate (ETRYNIT)	 $CH_3\text{-}CH_2\text{-}\overset{CH_2ONO_2}{\underset{CH_2ONO_2}{C}}—CH_2ONO_2$	165.29^{n}	169.98	–4.7
17	Erythritol tetranitrate (ETN)	 $NO_2OCH_2\text{-}\underset{ONO_2}{CH}\text{-}\overset{ONO_2}{CH}\text{-}CH_2ONO_2$	160.25^{n}	164.28	–4.0
18	1,1- Dinitronitroethane	$CH_3CH(NO_2)_2$	197.15^{t}	204.04	–6.9
19	2-Methyl-1,1,1,3-tetranitropropane (MeTENPr)	 $O_2N—\overset{NO_2}{\underset{NO_2}{C}}—\underset{CH_3}{CH}—CH_2—NO_2$	175.7^{n}	177.76	–2.1
20	1,1,1,2,2-Pentanitropropane (PNPr)	 $O_2N—\overset{NO_2}{\underset{NO_2}{C}}—\overset{NO_2}{\underset{NO_2}{C}}—CH_3$	166.1^{n}	174.91	–8.8
	The rms deviation / kJ mol^{-1}				8.8
	The average absolute deviation / kJ mol^{-1}				6.9

(rms) and the average absolute deviations of 9.8 and 7.4 kJ mol^{-1}, respectively. Moreover, the estimated activation energy by new correlation is more than 20 kJ mol^{-1} of the reported values only for two energetic compounds. As seen in Table 1, the deviations for experimental values are too high, e.g. compound numbers 24, 50 and 80. However, the best optimized values were derived for $E^{+}_{non-add}$ and $E^{-}_{non-add}$ using multiple linear regression method [38].

Table 2 indicates statistical parameters of Eq. (1), which allows comparing the relative weight of the variables in the model. Standard error shows a measure of the precision of the estimation of a coefficient. It can determine precision over repeated measurements. The P value can assess the significance of an observed effect or variation. For P value less than 0.05, it may confirm that the observed effect is not due to random variations and the effect is significant. Thus, suitable statistical parameters and good R^2 value, i.e. 0.92, validate that the predicted results of new method are in good agreement with experimental values.

The predicted activation energies for some complex energetic compounds, e.g. 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane (TEX), 2,4,6-tris(2,4,6-Trinitrophenyl)-1,3,5-triazine (TPT) and 1-(2,4,6-rinitrophenyl)-5,7-dinitrobenzotriazole (BTX), are given also in Table 3. As seen in Table 3, the new method gives relatively good results, which confirm the reliability of new method. Although experimental data were obtained from various methods such as DSC, SMM, TGA, DTA, NMR, IR and manometry, the predicted results in both Tables 1 and 3 are consistent with various experimental methods especially SMM method. Introduction of an amino group into a benzene ring containing a nitro group can enhance the thermal stability of explosives. Among various nitro derivatives of benzene, DATB and TATB have qualified as heat resistant explosives [1]. The predicted activation energy for both DATB and TATB is close to corresponding experimental values and higher than PAM. Due to the existence of large deviations for experimental values of some thermally stable explosives such as NONA, the predicted values are satisfactory. Tables 1 and 3 contain some well-known heat resistant polynitro arenes such as *N*,*N*-bis(2,4-dinitrophenyl)-2,4,6-trinitroaniline (NTFA), 3,3′-diamino-2,2′,4,4′,6,6′-hexanitrobiphenyl (DIPAM) and 2,2′,2″,4,4′,4″,6,6′,6″-nonanitro-*m*-terphenyl (NONA), which are highly thermostable and technologically exploited explosives. They have wide applications such as downhole well, achieving stage separation in space rockets, seismic experiments on the moon and booster explosives in space technology [35].

Liquid and solid phases are the state of thermal decomposition of energetic compounds. The influence of the condensed phase is expected to make itself felt in the reactivity through the changed character of bond hybridization of the molecule because of the presence of intermolecular interactions [32]. For the formation of the activated complex, the hinder influence of the closely arranged molecules within the crystal should be considered in solid phase decompositions [32]. Although the respective primary nitramines thermolysis is considered to have an autoprotolytic bimolecular course, the new method can be easily used for both primary and secondary nitramines.

Homolysis of the N–NO_2 bond as the primary fragmentation in thermolysis of the secondary amines in the condensed phase may be important for $E^{+}_{non-add}$ and $E^{-}_{non-add}$ under certain mentioned conditions. The presence of –NNO_2 in cyclic nitramine containing small ring provides a suitable path for decomposition of energetic compound with respect to –CNO_2. For TNAZ and its derivatives, it was found that the N–NO_2 fission is the convenient pathway in the kinetics and thermodynamic properties of their decomposition [39], which is consistent with $E^{-}_{non-add}$.

The present method can be programmed for designing a new energetic compound on the basis of $E^{+}_{non-add}$ and $E^{-}_{non-add}$ [40, 41]. Quantum mechanical methods have been also used to study thermal decomposition of some energetic compounds [42, 43]. In contrast to quantum mechanical methods, there is no need to use high speed computer and special computer codes. For some classes of energetic compounds, it is possible to correlate activation energy and the other related decomposition properties, e.g. the onset temperatures of nitro aromatic compounds [44].

Conclusions

A novel reliable simple correlation has been introduced to predict activation energy of energetic compounds containing –NNO_2, –ONO_2, –CNO_2 or –NNO groups. It is based on the number of carbon atoms and hydroxyl groups as well as two non-additive functions $E^{+}_{non-add}$ and $E^{-}_{non-add}$. As shown in Tables 1 and 3, the predictions for 106 (corresponding to 131 measured values) molecules provide reliable results with respect to experimental data. Since different factors can influence activation energy of an energetic compound, the main intent in this work was to investigate the likelihood of a generalized method to evaluate it. There is no need to use any experimental data or computed values in the new model. Equation (1) shows that it is possible to predict activation energies of new energetic compounds for which no data exist.

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