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New and reliable model for prediction of autoignition temperature of organic compounds containing energetic groups

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ABSTRACT

Autoignition temperature (AIT) is one of the most important safety specifications used to characterize the hazard potentials of a chemical substance. A simple model is introduced for reliable prediction of the AIT of organic compounds containing energetic functional groups nitro, nitrate, nitramine, and peroxide. It requires the only molecular structure of organic energetic compounds without using complex molecular descriptors and computer codes where they need expert users. Model building has been constructed on the basis of the measured AIT of 45 organic energetic compounds and compared with the predicted results of the best available group additivity method. For 9 compounds with unlike and complex molecular structures, the new model has also been checked that gives good predictions. The root mean square (RMS) deviations of the new model and group additivity method are 47.45 and 194.25 K, respectively, for 54 compounds (corresponding to 111 data points).

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1. Introduction

Autoignition temperature (AIT) is the lowest temperature in which a combustible material will produce hot-flame ignition in the air at atmospheric pressure without using an external energy source such as spark or flame (Bond, 1991). An exothermic oxidative reaction can be initiated spontaneously at the AIT. Thus, the AIT is one of the most important safety specifications used to characterize the hazard potentials of a chemical substance. The leak of organic compounds with low values of the AIT of organic compounds is one of the incidents of fire disasters. The experimental determination of the AIT is laborious and even may be impossible for some hazardous compounds because the measurement of the AIT depends on chemical and physical properties of the substance as well as test pressure, oxygen concentration, the volume and the material of the vessel used in the method. Differences of the reported values of the AIT of a specific compound in different kinds

of literature may be as much as 300 K (Chen et al., 2009; Keshavarz et al., 2013a). The AIT of hydrocarbons results from free radical reactions. The stability of free radical can be easily determined by oxidation of a desired compound. Thus, the ease of free radical formation and oxidation depend on the stability of forming radical.

Quantitative structure–property relationship (QSPR) (Bagheri et al., 2012; Borhani et al., 2016; Gharagheizi, 2011; Kim et al., 2002; Lazzús, 2011; Pan et al., 2008, 2009; Suzuki et al., 1992) and structural group contribution (SGC) (Albahri, 2003; Albahri and George, 2003; Chen et al., 2009) methods are two different approaches, which have been used to predict the AIT of different classes of organic compounds. Most of QSPR methods require special software such as Dragon (Mauri et al., 2006) and unusual molecular descriptors the same as topological indices, quantum chemical parameters, and electrostatic indices. It is important to use an appropriate dataset of different molecular structures because the compounds with similar molecular structure in training set of the QSPR procedure should be used as test set.

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The SGC methods are suitable pathways to predict the AIT of organic compounds. They have the advantage that calculation of the AIT is possible of only the chemical structure of the desired compound. They can be used only for those compounds that their functional groups have been defined for the model development. They usually cannot be applied for isomeric compounds. The Artificial Neural Network-Group Contribution (ANN-GC) method has recently applied to evaluate of the AIT using 146 functional groups (Gharagheizi, 2011). This method requires too many weighting parameters and special software. A suitable method has been introduced for predicting the AIT of different classes of hydrocarbons based on their molecular structures (Keshavarz et al., 2013a).

It is important to know the values of the AIT for combustible compounds in order to control their behaviors during handling, transportation and storing. Determination of the AIT by experiment is very laborious for some classes of organic compounds containing dangerous properties such as detonation (Agrawal, 2010; Klapötke, 2015), toxicity (Keshavarz et al., 2012; Keshavarz and Pouretedal, 2013; Pouretedal and Keshavarz, 2011), and an explosion of vapors of organic materials in air (Keshavarz and Ghanbarzadeh, 2011; Keshavarz et al., 2011; Pakdehi et al., 2015, 2014), e.g. rocket liquid fuels. Organic compounds containing energetic functional groups nitro, nitrate and peroxide are widely used in chemical industries as important classes of energetic materials (Agrawal, 2010; Klapötke, 2015). Due to the importance and different behavior of the AIT as well as difficulty of the experimental determination of the AIT for various classes of these categories of energetic materials, it is important to have a reliable and simple model for the explanation and prediction of their AIT. Different structural features can affect the mechanism of oxidation in the AIT of energetic compounds. For safety purposes, predicting AIT of a new or desirable energetic compound can reduce the costs associated with its synthesis, test, and evaluation. The purpose of this work is to introduce a novel method for prediction of the AIT of organic compounds containing energetic functional groups nitro, nitrate, and peroxide. This approach is consistent with different behaviors of free radical for decreasing or increasing of the AIT. The predicted results of the new method are compared to the estimated values of SGC method of Chen et al. (2009) as one of the best available methods.

2. Materials and methods

All databases usually reported the values of AIT of organic energetic compounds with no information of the used experimental method. Thus, development of a new model should estimate AIT values consistent with different authoritative sources. Since different values of AIT for a specific energetic compound may be reported in the literature, up to several hundred Kelvin (Chen et al., 2009; Keshavarz et al., 2013a), the reported data from different sources should be used. Fortunately, deviations are large only for little compounds. The values of 111 measured data corresponding to the AIT of 54 compounds were collected from diverse sources belong to different categories of energetic compounds have been chosen to derive and test a new correlation. Among different classes of organic energetic compound, at least one compound containing complex molecular structure from various categories is chosen to check the validity of the new method. Thus, 45 and 9 compounds have been selected as model building and external validation sets. Table 1 shows the experimental data of 45 organic energetic compounds containing functional groups nitro, nitrate, nitramine, and peroxide, corresponding to 92 measured data, which were taken from different sources such as DIPR 801 (Rowley et al., 2010). These were used to derive the new correlation that holds different structural moieties affecting the values of the AIT. Remaining 9 compounds with unlike and complex molecular structures have also been used to check the validity of the new correlation.

3. Results and discussion

3.1. Development of the new model

The study of the AIT of various energetic compounds reveals that there is a complex dependency on the molecular structure of the compound. It was found that the same as previous works for estimation of flammability of some classes of organic compounds (Keshavarz, 2012; Keshavarz and Ghanbarzadeh, 2011; Keshavarz et al., 2013a,b, 2016), it was found that elemental composition has the major contribution, which should be considered. Among different atoms, the numbers of carbon and oxygen atoms have the major contribution. Since the presence of the other atoms cannot improve the coefficient of determination (R^2) value, their contributions are neglected. Besides the contribution of elemental composition for predicting AIT of a desired energetic compound, it is essential to consider some structural parameters that may increase or decrease the predicted AIT base on elemental composition. Therefore, the optimized correlation using statistical analyses (multiple regressions (Palm, 2011)) for organic compounds containing energetic groups can be expressed as follows:

$$\begin{aligned} \text{AIT} = & 1095.27 - 5213.22(n_C/\text{MW}) - 13218.7(n_O/\text{MW}) \\ & + 82.1732 \text{AIT}_{\text{SPG}}^+ - 136.609 \text{AIT}_{\text{SPG}}^- \end{aligned} \quad (1)$$

where AIT is in K; n_C and n_O are the number of carbon and hydrogen atoms, respectively; MW is the molecular weight of a desired organic energetic compound; $\text{AIT}_{\text{SPG}}^+$ and $\text{AIT}_{\text{SPG}}^-$ are two correcting functions in this equation that are related to the presence of specific polar energetic groups under certain conditions.

$\text{AIT}_{\text{SPG}}^+$ and $\text{AIT}_{\text{SPG}}^-$ can adjust larger and lower high deviations of the predicted AIT on the basis of two ratios of n_C/MW and n_O/MW from experimental data. The values of $\text{AIT}_{\text{SPG}}^+$ and $\text{AIT}_{\text{SPG}}^-$ are given in Table 2. As seen in Eq. (1), the coefficients n_C/MW and n_O/MW have the negative values. Thus, increasing the values of n_C and n_O as well as decreasing MW can decrease the value of the AIT. Moreover, the contribution of $\text{AIT}_{\text{SPG}}^-$ is another way for decreasing of organic energetic compounds. More precautions should be considered for those organic energetic compounds containing large values of n_C/MW and n_O/MW in addition to the presence of $\text{AIT}_{\text{SPG}}^-$. As indicated in Table 2, the contribution of $\text{AIT}_{\text{SPG}}^-$ should be considered for cyclic and acyclic nitramines, which is consistent with the relatively high sensitivity of these compounds with respect to impact (Keshavarz, 2013), shock (Keshavarz et al., 2007) and electric spark (Keshavarz et al., 2009).

3.2. Reliability of the new model

Table 3 shows statistical parameters of Eq. (1) including regression coefficients, standard errors, P-values, as well as the upper and lower bounds of a 95% confidence interval. If the standard error of a coefficient is small relative to that, its variable is significant. Since P-value shows the probability that a parameter estimated from the measured data should have the value that was determined, the effect of a variable is significant. Thus, the observed effect is not due to random variations in a P-value of less than 0.05 (Billo, 2001). As seen in Table 3, all of the statistical parameters confirm that the proposed

Table 1 – Predictions of Eq. (1) for AIT (K) of organic energetic compounds (in the training set), compared to experimental data as well as the method of Chen et al. (2009).

Name	Formula	Exp. AIT (K)	Predicted AIT (K)			
			Eq. (1)	Dev.	Ref. (Chen et al., 2009)	Dev.
Nitromethane	CH_3NO_2	643.0 (Rowley et al., 2010)	658.58	15.58	671.68	28.68
		652.04 (Yaws, 1997)	658.58	6.54	671.68	19.64
		652.15 (Rowley et al., 2010)	658.58	6.43	671.68	19.53
		683.15 (McMillan, 1998)	658.58	−24.57	641.83	−41.32
		688.15 (McMillan, 1998)	658.58	−29.57	671.68	−16.47
		690.15 (Pohanish, 2012)	658.58	−31.57	671.68	−18.47
		691.15 (Larrañaga et al., 2016)	658.58	−32.57	671.68	−19.47
		691.483 (Lewis, 2008)	658.58	−32.91	671.68	−19.80
Nitroethane	$\text{C}_2\text{H}_5\text{NO}_2$	543.15 (Rowley et al., 2010)	685.92	142.77	641.83	98.68
		633.15 (Yaws, 1997)	685.92	52.77	641.83	8.68
		678.59 (Lewis, 2004)	685.92	7.33	641.83	−36.76
		683.15 (Anon, 2017b)	685.92	2.77	641.83	−41.32
		687.15 (Gokel, 2004)	685.92	−1.23	641.83	−45.32
		687.594 (Cheremisinoff, 1999)	685.92	−1.67	641.83	−45.76
		688.15 (Larrañaga et al., 2016)	685.92	−2.23	641.83	−46.32
1,3,5-Trinitroperhydro-1,3,5-triazine (RDX)	$\text{C}_3\text{H}_6\text{N}_6\text{O}_6$	470.15 (Harris, 1976)	462.64	−7.51	500.08	29.93
1-Nitropropane	$\text{C}_3\text{H}_7\text{NO}_2$	643.0 (Rowley et al., 2010)	704.66	61.66	612.90	−30.10
		693.15 (Larrañaga et al., 2016)	704.66	11.51	612.90	−80.25
		693.705 (Lewis, 2008)	704.66	10.96	612.90	−80.81
		694.15 (Pohanish and Greene, 2009)	704.66	10.51	612.90	−81.25
		694.26 (Yaws, 1997)	704.66	10.40	612.90	−81.36
		701.0 (Rowley et al., 2010)	704.66	3.66	612.90	−88.10
		755.15 (Patnaik, 2007)	704.66	−50.49	612.90	−142.25
1-Nitrobutane	$\text{C}_4\text{H}_9\text{NO}_2$	617.0 (Rowley et al., 2010)	636.14	19.14	585.53	−31.47
		633.15 (Rowley et al., 2010)	636.14	2.99	585.53	−47.62
1,2-Dichloro-4-nitrobenzene	$\text{C}_6\text{H}_3\text{Cl}_2\text{NO}_2$	693.15 (Anon, 2017b)	794.66	101.51	767.46	74.31
1,3-Dichloro-4-nitrobenzene	$\text{C}_6\text{H}_3\text{Cl}_2\text{NO}_2$	773.15 (Anon, 2017b)	794.66	21.51	767.46	−5.69
1,4-Dichloro-2-nitrobenzene	$\text{C}_6\text{H}_3\text{Cl}_2\text{NO}_2$	738.15 (Anon, 2017b)	794.66	56.51	767.46	29.31
1-Chloro-2,3-dinitrobenzene	$\text{C}_6\text{H}_3\text{ClN}_2\text{O}_4$	705.15 (Anon, 1991)	679.69	−25.46	631.08	−74.07
1-Chloro-2,4-dinitrobenzene	$\text{C}_6\text{H}_3\text{ClN}_2\text{O}_4$	705.15 (Rowley et al., 2010)	679.69	−25.46	631.08	−74.07
		705.372 (Yaws, 2003)	679.69	−25.68	631.08	−74.30
1-Chloro-3-nitrobenzene	$\text{C}_6\text{H}_4\text{ClNO}_2$	773.15 (Anon, 2017b)	728.81	−44.34	756.89	−16.26
1-Chloro-2-nitrobenzene	$\text{C}_6\text{H}_4\text{ClNO}_2$	760.15 (Anon, 2017b)	728.81	−31.34	756.89	−3.26
1-Chloro-4-nitrobenzene	$\text{C}_6\text{H}_4\text{ClNO}_2$	783.15 (Anon, 1991)	728.81	−54.34	756.89	−26.26
1,2-Dinitrobenzene	$\text{C}_6\text{H}_4\text{N}_2\text{O}_4$	743.15 (Anon, 2017b)	717.61	−25.54	620.15	−123.00
Nitrobenzene	$\text{C}_6\text{H}_5\text{NO}_2$	578.0 (Rowley et al., 2010)	749.28	171.28	746.10	168.10
		753.15 (Pohanish, 2012)	749.28	−3.87	746.10	−7.05
		754.82 (Yaws, 1997)	749.28	−5.54	746.10	−8.72
		755.15 (Larrañaga et al., 2016)	749.28	−5.87	746.10	−9.05
		755.37 (Lewis, 2004)	749.28	−6.09	746.10	−9.27
		769.15 (Smallwood, 2012)	749.28	−19.87	746.10	−23.05
4-Nitrophenol	$\text{C}_6\text{H}_5\text{NO}_3$	556.15 (Pohanish, 2012)	584.94	28.79	807.53	251.38
2-Nitroaniline	$\text{C}_6\text{H}_6\text{N}_2\text{O}_2$	794.15 (Rowley et al., 2010)	800.29	6.14	656.06	−138.09
		794.261 (Yaws, 2003)	800.29	6.03	656.06	−138.20
3-Nitroaniline	$\text{C}_6\text{H}_6\text{N}_2\text{O}_2$	794.15 (Pohanish and Greene, 2009)	800.29	6.14	656.06	−138.09
		794.15 (Pohanish and Greene, 2009)	800.29	6.14	656.06	−138.09
		849.82 (Yaws, 1997)	800.29	−49.53	656.06	−193.76
		850.0 (Rowley et al., 2010)	800.29	−49.71	656.06	−193.94
4-Nitroaniline	$\text{C}_6\text{H}_6\text{N}_2\text{O}_2$	783.15 (Pohanish, 2012)	800.29	17.14	656.06	−127.09
		849.82 (Yaws, 1997)	800.29	−49.53	656.06	−193.76
		850.0 (Rowley et al., 2010)	800.29	−49.71	656.05	−193.95
N-Methyl-N,2,4,6-tetranitroaniline (Tetryl)	$\text{C}_7\text{H}_5\text{N}_5\text{O}_8$	439.15 (Harris, 1976)	394.73	−44.42	501.93	62.78
2-Methyl-3,4-dinitrophenol	$\text{C}_7\text{H}_6\text{N}_2\text{O}_5$	613.15 (Anon, 2017b)	577.15	−36.00	595.03	−18.12
2-Methyl-4,6-dinitrophenol	$\text{C}_7\text{H}_6\text{N}_2\text{O}_5$	613.15 (Pohanish and Greene, 2009)	577.15	−36.00	595.03	−18.12
1-Methyl-2-nitrobenzene	$\text{C}_7\text{H}_7\text{NO}_2$	578.15 (Pohanish and Greene, 2009)	635.92	57.77	650.72	72.57
		693.15 (Anon, 2017b)	635.92	−57.23	650.72	−42.43

– Table 1 (Continued)

Name	Formula	Exp. AIT (K)	Predicted AIT (K)			
			Eq. (1)	Dev.	Ref. (Chen et al., 2009)	Dev.
1-Methyl-3-nitrobenzene	$C_7H_7NO_2$	578.0 (Rowley et al., 2010)	635.92	57.92	650.72	72.72
		663.15 (Yaws, 1997)	635.92	−27.23	650.72	−12.43
		713.0 (Anon, 2017a)	635.92	−77.08	731.32	18.32
1-Methyl-4-nitrobenzene	$C_7H_7NO_2$	616.0 (Rowley et al., 2010)	635.92	19.92	650.72	34.72
		663.15 (Rowley et al., 2010)	635.92	−27.23	650.72	−12.43
		723.15 (Pohanish and Greene, 2009)	635.92	−87.23	650.72	−72.43
(Nitromethyl) benzene	$C_7H_7NO_2$	578.15 (Pohanish and Greene, 2009)	635.92	57.77	716.75	138.60
1,3-Dimethyl-5-nitrobenzene	$C_8H_9NO_2$	647.0 (Rowley et al., 2010)	643.99	−3.01	562.77	−84.23
2-(sec-Butyl)-4,6-dinitrophenol	$C_{10}H_{12}N_2O_5$	616.0 (Rowley et al., 2010)	602.66	−13.34	551.07	−64.93
2-Nitro-1,1'-biphenyl	$C_{12}H_9NO_2$	452.15 (Gokel, 2004)	443.14	−9.01	725.66	273.51
		453.15 (Larrañaga et al., 2016)	443.14	−10.01	725.66	272.51
Ethyl nitrate	$C_2H_5NO_3$	358.15 (Gokel, 2004)	408.30	50.15	573.91	215.76
Nitroglycerine	$C_3H_5N_3O_9$	543.15 (Bond, 1991)	502.28	−40.87	518.72	−24.43
		652.15 (Rowley et al., 2010)	502.28	−149.87	518.72	−133.43
Isopropyl nitrate	$C_3H_7NO_3$	448.15 (Bond, 1991)	432.03	−16.12	580.22	132.07
n-Propyl nitrate	$C_3H_7NO_3$	448.15 (Lewis, 2008)	432.03	−16.12	549.93	101.78
		449.15 (Larrañaga et al., 2016)	432.03	−17.12	549.93	100.78
		450.15 (Pohanish and Greene, 2009)	432.03	−18.12	549.93	99.78
Pentaerythritol tetranitrate	$C_5H_8N_4O_{12}$	433.15 (Harris, 1976)	510.80	77.65	710.62	277.47
		483.15 (Pohanish, 2012)	510.80	27.65	710.62	227.47
n-Pentyl nitrate (n-amyl nitrate)	$C_5H_{11}NO_3$	468.15 (Bond, 1991)	464.50	−3.65	511.99	43.84
		483.15 (Bond, 1991)	464.50	−18.65	511.99	28.84
Hydroperoxymethane	CH_4O_2	387.0 (Rowley et al., 2010)	435.88	48.88	644.30	257.30
Ethaneperoxoic acid (peracetic acid)	$C_2H_4O_3$	383.15 (Pohanish and Greene, 2009)	436.28	53.13	652.72	269.57
		471.15 (Pohanish, 2012)	436.28	−34.87	652.72	181.57
		473.15 (Cheremisinoff, 1999)	436.28	−36.87	652.72	179.57
Hydroperoxyethane	$C_2H_6O_2$	385.0 (Rowley et al., 2010)	500.69	115.69	615.26	230.26
1-Hydroperoxybutane	$C_4H_{10}O_2$	633.15 (Rowley et al., 2010)	569.82	−63.33	562.35	−70.80
2-Hydroperoxy-2-methylpropane	$C_4H_{10}O_2$	360.15 (Pohanish and Greene, 2009)	364.90	4.75	648.41	288.26
		366.15 (Anon, 2011)	364.90	−1.25	648.41	282.26
Methyl ethyl ketone peroxide	$C_8H_{18}O_6$	663.15 (Bond, 1991)	683.34	20.19	489.78	−173.37
1-Hydroperoxy-2-isopropylbenzene	$C_9H_{12}O_2$	422.039 (Yaws, 2003)	476.05	54.01	723.36	301.32
1-Hydroperoxy-2-propylbenzene	$C_9H_{12}O_2$	515.0 (Rowley et al., 2010)	476.05	−38.95	569.70	54.70
1-Butyl-2-hydroperoxybenzene	$C_{10}H_{14}O_2$	504.0 (Rowley et al., 2010)	485.35	−18.65	546.20	42.20
Dodecanoic peroxyanhydride (dilauroyl peroxide)	$C_{24}H_{46}O_4$	279.15 (Bond, 1991)	374.83	95.68	1393.01	1113.86
		383.15 (Pohanish and Greene, 2009)	374.83	−8.32	1393.01	1009.86

Table 2 – Contribution of AIT_{SFG}^+ and AIT_{SFG}^- .

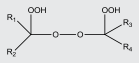
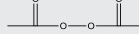

Organic compounds containing energetic groups	AIT_{SFG}^+	AIT_{SFG}^-	Condition
RNO_2	1.0	0	Nitroalkanes containing less than four carbon atoms as well as mononitro derivatives
$R-NNO_2$	0	1.5	–
Nitrobenzene	1.5	0	The attachment of only nitro groups or both nitro and amino groups to benzene ring
$RONO_2$	0	1.0	Mononitrate derivatives
$ROOH$	0	1.5	The attachment of $-OOH$ to tertiary carbon atom
	2	0	–
$Ar-OOH$	0	1.0	–
	0	2.0	–
	0	1.5	–

Table 3 – Regression coefficients of Eq. (1), as well as their standard deviations (sd), P-values, and confidence intervals.

Descriptor	Coefficients	sd	P-value	Lower bound (95%)	Upper bound (95%)
Intercept	1095.27	49.70	5.52E-24	994.82	1195.71
n_C/Mw	−5213.22	789.57	6.73E-08	−6809.01	−3617.43
n_O/Mw	−13218.7	1118.4	1.26E-14	−15479.1	−10958.4
AIT_{SPG}^+	82.1732	11.9218	2.65E-08	58.0784	106.268
AIT_{SPG}^-	−136.609	12.144	5.83E-14	−161.153	−112.065

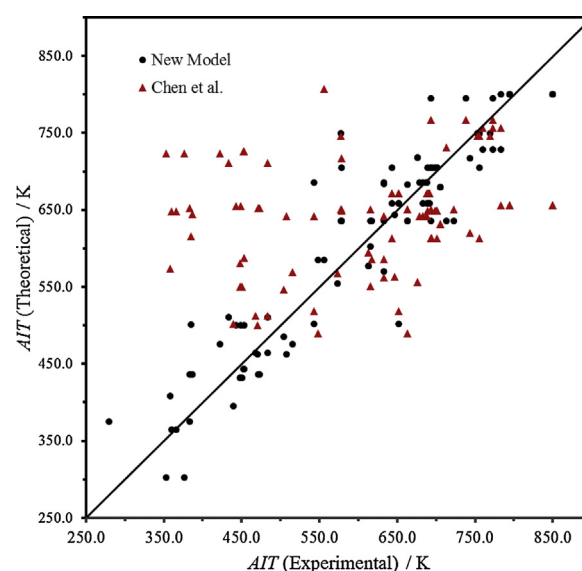
Table 4 – Predictions of Eq. (1) for AIT (K) of organic energetic compounds (in the test set), compared to experimental data as well as the method of Chen et al. (2009).

Name	Formula	Exp. AIT (K)	Predicted AIT (K)			
			Eq. (1)	Dev.	Ref. (Chen et al., 2009)	Dev.
2-Nitropropane	$C_3H_7NO_2$	578.15 (Rowley et al., 2010)	704.66	126.51	649.12	70.97
		689.15 (Pohanish and Greene, 2009)	704.66	15.51	649.12	−40.03
		694.15 (Gangolli, 1999)	704.66	10.51	649.12	−45.03
		698.15 (Rowley et al., 2010)	704.66	6.51	649.12	−49.03
		700.927 (Lewis, 2008)	704.66	3.74	649.12	−51.80
		700.15 (Larrañaga et al., 2016)	704.66	4.51	649.12	−51.03
		700.93 (Yaws, 1997)	704.66	3.73	649.12	−51.81
		701.15 (Armour, 2003)	704.66	3.51	649.12	−52.03
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)	$C_4H_8N_8O_8$	507.15 (Harris, 1976)	462.64	−44.51	642.09	134.94
2,4,6-Trinitrophenol (picric acid)	$C_6H_3N_3O_7$	573.15 (Pohanish, 2012)	554.61	−18.54	567.89	−5.26
2,4,6-Trinitrotoluene (TNT)	$C_7H_5N_3O_6$	548.15 (Harris, 1976)	585.11	36.96	489.64	−58.51
Nitrocellulose	$C_{12}H_{14}N_6O_{22}$	443.15 (Larrañaga et al., 2016)	500.37	57.22	654.74	211.59
		449.15 (Harris, 1976)	500.37	51.22	654.74	205.59
		453.15 (Pohanish and Greene, 2009)	500.37	47.22	587.66	134.51
Urea peroxide	$C_2H_{10}N_4O_4$	633.15 (Cheremisinoff, 1999)	684.22	51.07	–	–
Cyclohexanone peroxide	$C_{12}H_{22}O_6$	675.927 (Cheremisinoff, 1999)	718.12	42.19	555.97	−119.96
		676.15 (Pohanish and Greene, 2009)	718.12	41.97	555.97	−120.18
Benzoic peroxyanhydride (or benzoyl peroxide)	$C_{14}H_{10}O_4$	353.15 (Patnaik, 2007)	301.97	−51.18	723.08	369.93
		376.0 (Rowley et al., 2010)	301.97	−74.03	723.08	347.08

descriptors in Eq. (1) have a highly significant ability to predict the AIT.

Table 1 compares the predicted results of the new model with the estimated values of SGC method of Chen et al. (2009) as one of the best available methods. The predictive reliability of Eq. (1) has been tested for some organic energetic compounds with unlike and complex molecular structures, which have been given in Table 4. Comparison of the predicted results of the model and SGC method of Chen et al. (2009) have also been compared with experimental data. Table 5 shows a comparison between further statistical parameters of Eq. (4) for model building and the test dataset. Fig. 1 shows the linear relationship between the experimental and predicted values of AIT for all data points. As seen, the predictions of the model exhibit a lower dispersion with respect to the Chen et al. (2009) method. The accuracy of each new model can be visualized by dividing the absolute percent errors ($APE = 100 \times |AIT_{exp} - AIT_{pred}| / AIT_{exp}$) into some categories. In Fig. 2, the APE values for all 111 data points, obtained by the new model and the Chen et al. (2009) method, were categorized into ten sub-groups. If, for example, the $APE < 6$ considered as a milestone, it can be seen that between 111 data points, the new model predicts 72 data in this range, i.e. 65% of predictions are very accurate.

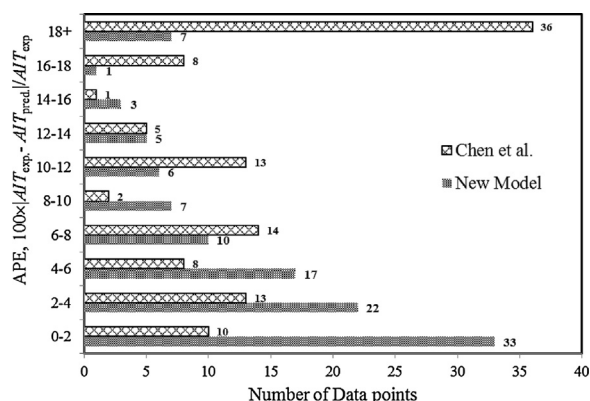
Root Mean Squared (RMS) error gives a reliable suggestion of the fitness of the model. It is independent of the distribution of data points. It should be low to ensure the predictive abil-

**Fig. 1 – The predicted AIT (K) using the developed model and the Chen et al. (2009) method versus experimental values for all 111 data points.**

ity (Gramatica, 2007). Mean Absolute Error (MAE) assesses the average size of errors when negative signs are ignored. These statistical parameters and maximum of error (Max Error) of these data as well as R^2 , F static and significant F are given in

Table 5 – Performance statistics of Eq. (1).

Data set	Data points	RMS	MAE	Max error	R ²	F statistic	Significance F
Train set	92	47.45	33.96	171.28	0.9123	104.038	1.39E-20
Test set	19	47.31	36.35	126.51	–	–	–

**Fig. 2 – The range of the absolute percent errors of Eq. (1) and the Chen et al. (2009) method for 111 data points.****Table 6 – Comparison of statistical parameters of Eq. (1) with the Chen et al. (2009) method (for the whole dataset).**

Method	Data points	RMS	MAE	Max error
Eq. (1)	111	47.42	34.37	171.28
Chen et al. (2009)	111	194.25	116.93	1113.9

Table 5. The values of RMS and MAE parameters for both sets are close to each other. Meanwhile, the value of Max Error in the test set is smaller than training set. Table 6 compares statistical parameters of RMS, MAE and Max Error of all 111 data points given in Tables 1 and 5 for the new and SGC methods (Chen et al., 2009). The values of RMS, MAE and Max Error by Eq. (1) are 47.42, 34.37 and 171.28 K, respectively. These statistical parameters with the method of Chen et al. (2009) are 194.25, 116.93 and 1113.9 K, respectively, which confirmed the high reliability of the new method.

4. Conclusions

This work was introduced a simple and reliable model for prediction of the AIT of organic energetic compounds. Since experimental data of the AIT of organic energetic compounds are scarce and expensive, Eq. (1) provides a reliable method for its prediction. Moreover, valuable insight into the structural significance and the AIT trends of organic energetic compounds can be provided by determining how susceptible individual structural features are to oxidative attack and autoignition. For designing of the new organic energetic compounds, the novel method can also be used to estimate their safety to burst into flames. As compared to the best available SGC method, i.e. Chen et al. (2009), the present model provides more reliable results and can be easily applied for different types of organic energetic compounds. Furthermore, in contrast to available QSPR methods, there is no need to use complex computer codes, unusual descriptors, and expert users.

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References

- Agrawal, J.P., 2010. *High Energy Materials: Propellants, Explosives and Pyrotechnics*. John Wiley & Sons.
- Albahri, T.A., 2003. Flammability characteristics of pure hydrocarbons. *Chem. Eng. Sci.* 58, 3629–3641.
- Albahri, T.A., George, R.S., 2003. Artificial neural network investigation of the structural group contribution method for predicting pure components auto ignition temperature. *Ind. Eng. Chem. Res.* 42, 5708–5714.
- Anon, 1991. *Chemical Safety Sheets: Working Safely with Hazardous Chemicals*. Springer, Netherlands.
- Anon, 2011. *Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards, Updated Version*. National Academies Press, Washington, D.C.
- Anon, 2017a. *Hazardous Chemical Database*. The University of Akron, Ohio.
- Anon, 2017b. *International Chemical Safety Cards (ICSDs). International Programme on Chemical Safety (IPCS)*.
- Armour, M.A., 2003. *Hazardous Laboratory Chemicals Disposal Guide, 3rd ed.* Lewis Publishers, Boca Raton, Florida.
- Bagheri, M., Borhani, T.N.G., Zahedi, G., 2012. Estimation of flash point and autoignition temperature of organic sulfur chemicals. *Energy Convers. Manage.* 58, 185–196.
- Billo, E.J., 2001. *Excel for Chemists: A Comprehensive Guide, 2nd ed.* Wiley, New York.
- Bond, J., 1991. *Sources of Ignition: Flammability Characteristics of Chemicals and Products*. Elsevier.
- Borhani, T.N.G., Afzali, A., Bagheri, M., 2016. QSPR estimation of the auto-ignition temperature for pure hydrocarbons. *Process Saf. Environ. Prot.* 103, 115–125.
- Chen, C.-C., Liaw, H.-J., Kuo, Y.-Y., 2009. Prediction of autoignition temperatures of organic compounds by the structural group contribution approach. *J. Hazard. Mater.* 162, 746–762.
- Cheremisinoff, N.P., 1999. *Handbook of Industrial Toxicology and Hazardous Materials*. CRC Press.
- Gangolli, S., 1999. *The Dictionary of Substances and Their Effects*. Royal Society of chemistry.
- Gharagheizi, F., 2011. An accurate model for prediction of autoignition temperature of pure compounds. *J. Hazard. Mater.* 189, 211–221.
- Gokel, G.W., 2004. *Dean's Handbook of Organic Chemistry*. McGraw-Hill, New York.
- Gramatica, P., 2007. Principles of QSAR models validation: internal and external. *QSAR Comb. Sci.* 26, 694–701.
- Harris, J., 1976. Autoignition temperatures of military high explosives by differential thermal analysis. *Thermochim. Acta* 14, 183–199.
- Keshavarz, M.H., 2012. Estimation of the flash points of saturated and unsaturated hydrocarbons. *Indian J. Eng. Mater. Sci.* 19, 269–278.
- Keshavarz, M.H., 2013. A new general correlation for predicting impact sensitivity of energetic compounds. *Propellants Explos. Pyrotech.* 38, 754–760.
- Keshavarz, M.H., Ghanbarzadeh, M., 2011. Simple method for reliable predicting flash points of unsaturated hydrocarbons. *J. Hazard. Mater.* 193, 335–341.

- Keshavarz, M.H., Gharagheizi, F., Ghanbarzadeh, M., 2013a. A simple correlation for prediction of autoignition temperature of various classes of hydrocarbons. *J. Iran. Chem. Soc.* 10, 545–557.
- Keshavarz, M.H., Moradi, S., Madram, A.R., Pouretedal, H.R., Esmailpour, K., Shokrolahi, A., 2013b. Reliable method for prediction of the flash point of various classes of amines on the basis of some molecular moieties for safety measures in industrial processes. *J. Loss Prev. Process Ind.* 26, 650–659.
- Keshavarz, M.H., Gharagheizi, F., Shokrolahi, A., Zakinejad, S., 2012. Accurate prediction of the toxicity of benzoic acid compounds in mice via oral without using any computer codes. *J. Hazard. Mater.* 237, 79–101.
- Keshavarz, M.H., Jafari, M., Kamalvand, M., Karami, A., Keshavarz, Z., Zamani, A., Rajaei, S., 2016. A simple and reliable method for prediction of flash point of alcohols based on their elemental composition and structural parameters. *Process Saf. Environ. Prot.* 102, 1–8.
- Keshavarz, M.H., Motamedoshariati, H., Pouretedal, H.R., Tehrani, M.K., Semnani, A., 2007. Prediction of shock sensitivity of explosives based on small-scale gap test. *J. Hazard. Mater.* 145, 109–112.
- Keshavarz, M.H., Pouretedal, H.R., 2013. Simple and reliable prediction of toxicological activities of benzoic acid derivatives without using any experimental data or computer codes. *Med. Chem. Res.* 22, 1238–1257.
- Keshavarz, M.H., Pouretedal, H.R., Semnani, A., 2009. Reliable prediction of electric spark sensitivity of nitramines: a general correlation with detonation pressure. *J. Hazard. Mater.* 167, 461–466.
- Keshavarz, M.H., Ramadan, A., Mousaviazar, A., Zali, A., Esmailpour, K., Atabaki, F., Shokrollahi, A., 2011. Reducing dangerous effects of unsymmetrical dimethyl hydrazine as a liquid propellant by addition of hydroxyethylhydrazine, part I, physical properties. *J. Energ. Mater.* 29, 46–60.
- Kim, Y.S., Lee, S.K., Kim, J.H., Kim, J.S., No, K.T., 2002. Prediction of autoignition temperatures (AITs) for hydrocarbons and compounds containing heteroatoms by the quantitative structure–property relationship. *J. Chem. Soc. Faraday Trans.*, 2087–2092.
- Klapötke, T.M., 2015. *Chemistry of High-Energy Materials*, 3rd ed. Walter de Gruyter GmbH, Berlin.
- Larrañaga, M.D., Lewis, R.J.S., Lewis, R.R., 2016. *Hawley's Condensed Chemical Dictionary*, 16th ed. Wiley, Hoboken, New Jersey.
- Lazzús, J.A., 2011. Autoignition temperature prediction using an artificial neural network with particle swarm optimization. *Int. J. Thermophys.* 32, 957–973.
- Lewis, R.J., 2008. *Hazardous Chemicals Desk Reference*. John Wiley & Sons.
- Lewis, R.J.S., 2004. *Sax's Dangerous Properties of Industrial Materials*, 11th ed. Wiley, Hoboken, New Jersey.
- Mauri, A., Consonni, V., Pavan, M., Todeschini, R., 2006. Dragon software: an easy approach to molecular descriptor calculations. *MATCH—Commun. Math. Comput. Chem.* 56, 237–248.
- McMillan, A., 1998. *Electrical Installations in Hazardous Areas*. Butterworth-Heinemann.
- Pakdehi, S.G., Ajdari, S., Hashemi, A., Keshavarz, M.H., 2015. Performance evaluation of liquid fuel 2-dimethyl amino ethyl azide (DMAZ) with liquid oxidizers. *J. Energ. Mater.* 33, 17–23.
- Pakdehi, S.G., Rezaei, S., Motamedoshariati, H., Keshavarz, M.H., 2014. Sensitivity of dimethyl amino ethyl azide (DMAZ) as a non-carcinogenic and high performance fuel to some external stimuli. *J. Loss Prev. Process Ind.* 29, 277–282.
- Palm, W.J., 2011. *Introduction to MATLAB for Engineers*, 3rd ed. McGraw-Hill, New York.
- Pan, Y., Jiang, J., Wang, R., Cao, H., 2008. Advantages of support vector machine in QSPR studies for predicting auto-ignition temperatures of organic compounds. *Chemometr. Intell. Lab. Syst.* 92, 169–178.
- Pan, Y., Jiang, J., Wang, R., Cao, H., Cui, Y., 2009. Predicting the auto-ignition temperatures of organic compounds from molecular structure using support vector machine. *J. Hazard. Mater.* 164, 1242–1249.
- Patnaik, P., 2007. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 3rd ed. Wiley, New Jersey.
- Pohanish, R.P., 2012. *Sittig's Handbook of Toxic and Hazardous Chemicals and Carcinogens*. William Andrew.
- Pohanish, R.P., Greene, S.A., 2009. *Wiley Guide to Chemical Incompatibilities*. John Wiley & Sons.
- Pouretedal, H., Keshavarz, M., 2011. Prediction of toxicity of nitroaromatic compounds through their molecular structures. *J. Iran. Chem. Soc.* 8, 78–89.
- Rowley, R., Wilding, W., Oscarson, J., Giles, N., 2010. *DIPPR® Data Compilation of Pure Chemical Properties*. Design Institute for Physical Properties, AIChE, New York.
- Smallwood, I., 2012. *Handbook of Organic Solvent Properties*. Butterworth-Heinemann.
- Suzuki, T., Ohtaguchi, K., Koide, K., 1992. Correlation and prediction of autoignition temperatures of hydrocarbons using molecular properties. *J. Chem. Eng. Jpn.* 25, 606–608.
- Yaws, C.L., 1997. *Handbook of Chemical Compound Data for Process Safety*. Gulf Professional Publishing.
- Yaws, C.L., 2003. *Yaws' Handbook of Thermodynamic and Physical Properties of Chemical Compounds*. Knovel, New York.