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Empirical Method for the Prediction of Heat of Formation of Organic High Energy Molecules

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ABSTRACT

An empirical method based on additive procedures is proposed for estimating the heats of formation of aliphatic, aromatic, and ring molecules containing nitro and other energetic groups at standard state. The method uses only molecular structural information. Calculation of heat of formation is carried out in three stages, first the heat of formation for gaseous state is calculated, followed by incorporation of heat of vapourisation/sublimation, and finally, corrections are done for interactions. Some interaction terms, based on hydrogen bonding strength for various compounds and experimental heat of formation of isomeric compounds, are also proposed. The results are in good agreement with the experimentally determined values. The method provides quick and sufficiently accurate values of heat of formation of organic high energy molecules.

Keywords: Heat of formation, enthalpy of vapourisation, enthalpy of sublimation, high energy molecule, group additivity

1. INTRODUCTION

Knowledge about heat of reaction is of paramount importance for proper designing of plants and equipment in any chemical process industry. It becomes even more critical while designing plants for hazardous reactions. Heat of formation data is generally used for the calculation of heat of reaction and is of importance to chemists developing new synthesis methods or new energetic molecules, as it enters into the calculation of explosive and propellant properties such as detonation velocity, detonation pressure, and specific impulse. A good number of methods, starting from simple additive methods coupled with a few thermodynamic correlations to advanced rigorous quantum mechanical approaches, are available for the estimation of heat of formation.

Additive methods such as developed by Benson¹, Joback and Reid², Cardozo³, Constantinou and Gani (CG method)⁴, group interaction contribution (GIC) method⁵, etc, are used for the calculation of heat of formation. The Joback and Reid method is not as popular as the Benson's method¹, but is very simple and easy to use. The Cardozo method³ is best suited for alkyl derivatives. The CG method⁴ claims to give better predictions but its applicability to high energy molecules is limited due to lack of data.

The calculation of heat of vapourisation/sublimation requires knowledge of critical temperature, critical pressure, normal boiling point, acentric factor, vapour pressure, etc. The Ambrose and Lydersen methods (In Liley's⁶, *et al.*) are the most popular methods

for obtaining the theoretical critical points. However, both the methods require knowledge of the boiling point.

Various methods are available for the prediction of normal boiling points, viz., Pailhes method, Joback method², CG method⁴, GIC method⁵, group vector space (GVS) method⁸, etc. Reynes and Thodos⁹, and Miller¹⁰ have proposed efficient methods for the determination of vapour pressure. The Lee-Kesler equation¹¹ is widely used for the prediction of acentric factor. The Edmister equation is also sometimes used when very high accuracies are not required. The Pitzer¹² *et al.* and Reid⁷, *et al.* methods are usually the choice for prediction of enthalpy of vapourisation. For the current work, only the heat of formation at standard state has been considered. There is scanty literature available on prediction of heat of fusion. Bondi¹³ has provided a method for calculating the same. However, this method does not provide very good accuracy. Usually, the Reid⁷, *et al.* equation for heat of fusion is extensively used.

The incorporation of molecular interaction parameters is rather limited and only a few could be found in the literature. Bourasseau¹⁴ has given the various types of major interactions and the corresponding energies for non-aromatic nitro compounds.

Most of the methods discussed above, were designed, tested, and used for petrochemicals which are mostly gases and light organic hydrocarbons. The methods have not been tested extensively on high-energy molecules, which in contrast to the petrochemicals, are highly viscous liquids and solids. In fact, almost all currently used military explosives are high-density solids. The current work aims at devising a proper algorithm using additive methods and standard thermodynamic correlations for estimating the heat of formation of high-energy molecules.

In the present work, calculation of heat of formation is done in three steps:

- Calculation of heat of formation for gaseous state at standard condition.

- Calculation of heat of vapourisation/sublimation.
- Incorporation of interaction energy.

2. METHODOLOGY

Of the many methods described in the literature, the Joback-Reid method² was chosen for the determination of gas-phase heat of formation because of its simplicity and availability of data for large number of groups. The CG method⁴ was also tested. However, it was found that the Joback² method gave better predictions compared to the CG method. Also the CG method has very limited data or group contribution values. The Joback correlation is:

$$\Delta H_{f,298}^{\circ} = 68.29 + \sum_{i=1}^n N_i \Delta_{Hi} \quad (1)$$

where $\Delta H_{f,298}^{\circ}$ (kJ/mole) is the gas-phase enthalpy of formation at 298.15 K and 1 atmosphere; n , the number of different groups; N_i , the number of a particular groups t present in the molecule; Δ_{Hi} is the group contribution value for the i^{th} group.

The next step is the critical step of calculation of the enthalpy of vapourisation for liquid or enthalpy of sublimation for solids. The following Pitzer¹², *et al.* relation modified by Reid⁷ *et al.* is used for the present system:

$$\Delta H_v = RT_c \left[7.08(1 - T_r)^{0.354} + 10.95(1 - T_r)^{0.456} \right] \quad (2)$$

where Δ_{Hv} (kJ/mole) is the enthalpy of vapourisation; R , the gas constant (0.008314 kJ/mol K); T_c , the critical temperature (K); T_r , the reduced temperature and ω , the acentric factor. Critical temperature and pressure were calculated using the Lydersen's equations as:

$$T_c = \frac{T_b}{0.567 + \sum \Delta_T - \left(\sum \Delta_T \right)^2} \quad (3)$$

$$P_c = \frac{0.101325M}{\left(0.34 + \sum \Delta_p \right)} \quad (4)$$

where Δ_T and Δ_p are the Lydersen group contribution towards critical temperature and pressure, respectively

and M being the molecular weight. Two methods were found useful for the prediction of acentric factors. In the Lee-Kesler method¹¹, the following equations were solved to obtain the acentric factor:

$$\ln P_r^{sat} = \ln P_r^{sat^0} + \omega \ln P_r^{sat^1} \quad (5)$$

$$\ln P_r^{sat^0} = 5.92714 - \frac{6.09648}{T_r} - 1.28862 \ln T_r + 0.169347 T_r^6 \quad (6)$$

$$\ln P_r^{sat^1} = 15.25180 - \frac{15.68750}{T_r} - 13.47210 \ln T_r + 0.43577 T_r^6 \quad (7)$$

$$\omega = -\ln\left(P_r^{sat}\right)_{T_r=0.7} - 1.0000 \quad (8)$$

where P_r^{sat} , is the reduced vapour pressure. Alternatively, Edmister equation⁷ may be used for the prediction of acentric factor.

$$\omega = \frac{3}{7} \left(\frac{\theta}{1-\theta} \right) \ln P_c - 1 \quad (9)$$

In Eqn (9), $\theta = T_b/T_c$ and P_c is the pressure in atmosphere units.

There are a number of methods available for the prediction of normal boiling point, the most accurate being the Pailhes method:

$$T_b = T \frac{\ln P_c + (1-\theta^{-1}) \ln \left(\frac{1}{p} \right)}{\ln P_c} \quad (10)$$

where T is any temperature less than T_b and p , the corresponding vapour pressure. In the absence of data, the Joback method⁷ may be used for reasonable predictions of normal boiling points.

$$T_b = 198 + \sum \Delta_b \quad (11)$$

In Eqn (11), Δ_b is the Joback group increment towards boiling point. Most of the equations reported are obtained from regression of experimental values of large number of compounds.

Prediction of heat of sublimation of solids is even more difficult task. It is assumed in this study

that heat of sublimation, ΔH_s may be treated as the sum of enthalpy of vapourisation, ΔH_v and enthalpy of fusion, ΔH_{fus} . ΔH_v may be obtained by the procedure described above. The atomic group contribution method of Bondi¹³ and Chickos⁶, *et al.* may be used for the prediction of ΔH_{fus} . However, the accuracy does not warrant the use of these methods and a simpler assumption of Reid⁷, *et al.*, *ie*, $\Delta H_f = \Delta H_v/3$ is used in the present study.

Any real molecule has a number of interactions, both intermolecular as well as intramolecular. The nature of interactions may increase the heat of formation of the compound (eg, in case of hydrogen bonding) or decrease the heat of formation (eg, bulky groups in adjacent positions).

The following interaction energies were taken for calculation of heat of formation of compounds reported herein:

- Each H atom connected to O atom—addition of 7 kcal/mole.
- Each H atom connected to N atom—addition of 4.5 kcal/mole.
- Every two nitro groups attached to the same C —reduction of 7 kcal/mole.
- Adjacent nitro groups in aromatic moiety—reduction of 8 kcal/mole.
- Nitro groups attached to adjacent C atoms—reduction of 5 kcal/mole.
- Two nitro groups, one attached to C atom and the other attached to O atom and separated by one C atom—reduction of 5 kcal/mole.

The basis for Eqns (1) and (2) is that, the hydrogen bond strength is of the order of 4.0-7.5 kcal/mole¹⁶. A higher strength is assigned to the hydrogen bond via O atom whereas a lower value is assigned to the hydrogen bond via N atom, as the electronegativity of O is higher than N . The interaction value in Eqn (3) for nitro groups attached to same C atom has been derived from experimental value of heat of formation for tetranitromethane.

The interaction value in Eqn (4) was derived from the experimental heat of formation of isomeric aromatic nitro compounds. Finally, the interaction value in Eqns (5) and (6) was taken from Bourasseau¹⁴.

Even though the results have been reported for the standard state, these can be easily converted to other temperatures. Heat of vapourisation, and hence, the heat of formation at various temperatures can be calculated by Watson procedure¹⁵.

$$\Delta H_v^{(2)} = \Delta H_v^{(1)} \left[\frac{1 - T_r^{(2)}}{1 - T_r^{(1)}} \right]^{0.38} \quad (12)$$

where $\Delta H_v^{(2)}$ is the heat of formation at any reduced temperature $T_r^{(2)}$ and $\Delta H_v^{(1)}$ is the heat of vapourisation at standard state ($T_r^{(1)} = 298.15$ K).

3. THEORETICAL CALCULATION OF $\Delta H_{f \text{ solid}}$ OF TATB

From Eqns (11), (4) and (3), $T_b=1061$ K, $P_c=32.7$ MPa, $T_c=1350$ K respectively.

From Eqn (1), $\Delta H_{f298}^0 = 19.37$ kcal/mole

From Eqn (2), $\Delta H_v = 71.22$ kcal/mole

hence, $\Delta H_f = 23.74$ kcal/mole.

Therefore, $\Delta H_{f \text{ solid}} = 19.37 - 23.74 = -4.37$ kcal/mole (without interaction).

Interaction energy = 6×4.5 (item 2 of interaction energies given above).

Actual $\Delta H_{f \text{ solid}} = -4.37 - (6 \times 4.5) = -31.37$ kcal/mole.

4. RESULTS & DISCUSSION

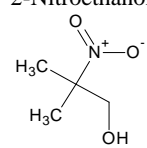
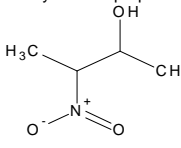
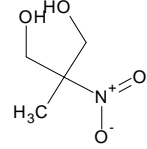
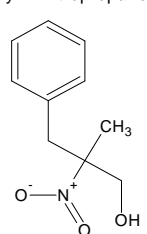
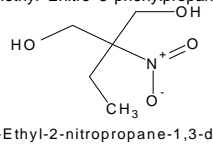
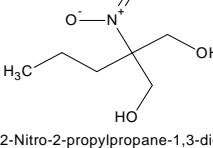
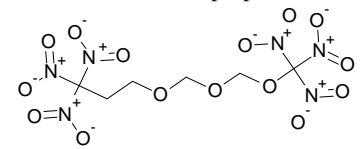
The procedure described above was implemented in C programming language. The proposed procedure has been tested on a large number of molecules with fairly good results. Errors were usually less than ± 5 to 10 kcal/mole which may be considered as very encouraging, given the fact that the procedure uses only molecular structural information. Table 1¹⁷⁻²⁰

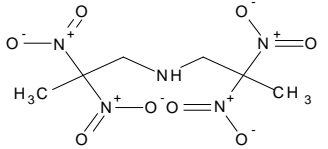
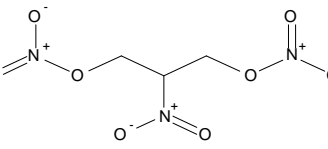
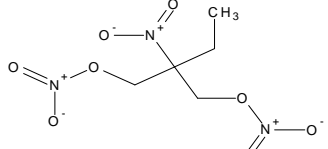
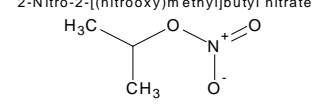
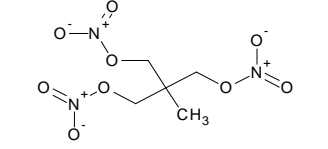
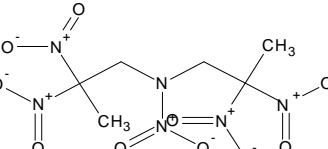
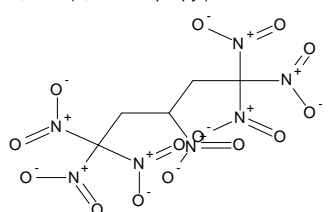
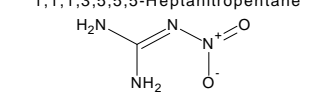
shows comparative data of experimental and predicted heat of formation of three classes of molecules of aliphatic, aromatic, and ring structures, containing nitro and other energetic groups¹⁷⁻²⁰. Errors for molecules containing $-O-NO_2$ were found to be on a higher side. This was due to the nonavailability of group contribution data for this class and instead, values of $-O-$ and NO_2 were taken. Also, contribution for tertiary *N* in ring structure is not available. Hence, the value was taken for non-ring tertiary *N*.

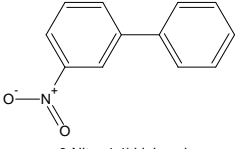
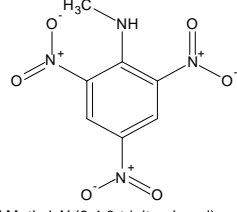
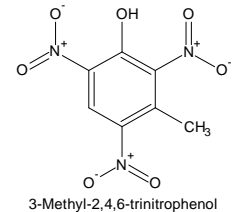
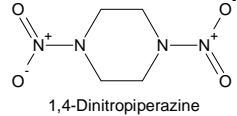
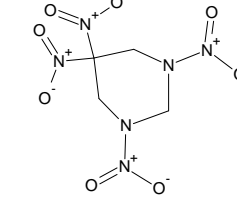
The assumption gave good results for molecules having single ring structure (eg, HMX, RDX, etc), however, for molecules having multiple rings where the ring strain becomes too large to accommodate non-ring tertiary *N* contribution, higher errors were obtained. Certain molecules, like 1,4-dintropiperazine, naphthalene derivatives, etc are giving comparatively lower predictions. This is due to the highly symmetrical structures, which increases the stability of the molecule, and hence, the heat of formation. The method tries to differentiate between isomers when there is a difference in intramolecular interactions. However, to get more accurate results for isomers, newer approaches like the GSV and GIC methods^{5,8} are suggested.

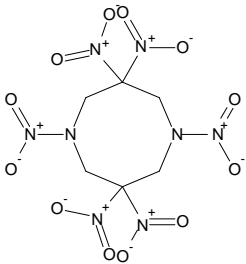
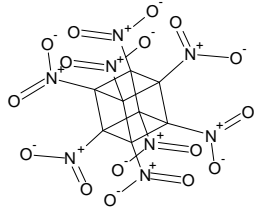
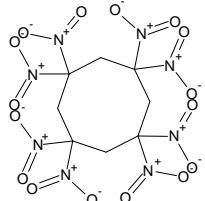
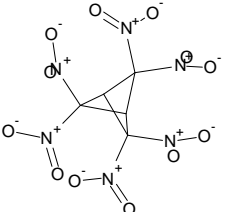
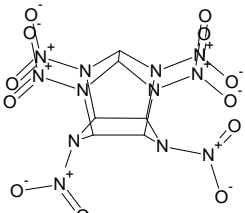
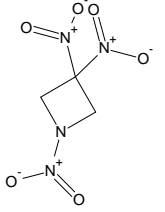
Higher errors are also obtained in compounds containing secondary amine with nitro group(s) in adjacent positions. This is due to the poor hydrogen bonding (due to strong-I effect) and steric clouding of the nitro groups. Predictions have also been done for certain polynitro compounds for which no experimental data is available. The values suggested for octanitrocubane, CL-20 and 1,3,3-trinitroazetidine (TNAZ) should be taken with a little caution as the molecules have very high ring strains. The reason for the divergence for phenolic compounds containing nitro groups is not clear. The procedure outlined in the paper yields errors that are almost of the same order when compared to those given by Bourasseau procedure¹⁴. The proposed procedure is superior to the Bourasseau procedure in the sense that the latter treats only non-aromatic nitro compounds.

Table 1. Comparison of experimental and predicted values of heat of formation^{14,17}

Molecule	State	Experimental ΔH_f (kcal/mole)	Theoretical ΔH_f (kcal/mole)	Error (kcal/mole)
<i>ALIPHATIC STRAIGHT-CHAIN COMPOUNDS</i>				
Methylnitrite	Gas	-15.79±0.25 ¹⁷	-17.80	2.01
Nitromethane	Liquid	-27.03±0.15 ¹⁷	-27.47	0.44
Nitroethane	Liquid	-34.32±0.26 ¹⁷	-32.77	-1.55
1-Nitropropane	Liquid	-40.35±0.30 ¹⁷	-37.66	-2.69
2-Nitropropane	Liquid	-43.09±0.20 ¹⁷	-38.92	-4.17
1-Nitrobutane	Liquid	-46.00±0.33 ¹⁷	-42.78	-3.22
2-Nitrobutane	Liquid	-49.59±0.37 ¹⁷	-44.03	-5.56
2-Nitroethanol	Liquid	-83.83±0.56 ¹⁷	-77.94	-5.89
	Solid	-98.02±0.41 ¹⁷	-93.92	-4.10
2-Methyl-2-nitropropan-1-ol				
	Liquid	-93.2±1.2 ¹⁷	-90.51	-2.69
3-Nitrobutan-2-ol				
	Solid	-138.62±0.67 ¹⁷	-139.72	1.10
2-Methyl-2-nitropropane-1,3-diol				
	Solid	-83.1±1.1 ¹⁷	-69.04	-14.06
2-Methyl-2-nitro-3-phenylpropan-1-ol				
	Solid	-145.23 ¹⁴	-144.74	-0.49
2-Ethyl-2-nitropropane-1,3-diol				
	Solid	-149.43±0.70 ¹⁷	-149.78	0.35
2-Nitro-2-propylpropane-1,3-diol				
1,2-Dinitroethane	Solid	-42.00±0.29 ¹⁷	-41.29	-0.71
1,1-Dinitropropane	Liquid	-40.77 ¹⁴	-36.61	-4.16
	Solid	-142.70 ¹⁴	-137.48	-5.22
1,1,1,9,9,9-Hexanitro-4,6,8-trioxononane				

Molecule	State	Experimental ΔH_f (kcal/mole)	Theoretical ΔH_f (kcal/mole)	Error (kcal/mole)
 <i>N,N</i> -Bis(2,2-dinitropropyl)amine	Solid	-63.40 ¹⁴	-53.76	-9.64
 2-Nitro-3-(nitrooxy)propyl nitrate	Liquid	-88.60 ¹⁴	-101.65	13.05
 2-Nitro-2-[(nitrooxy)methyl]butyl nitrate	Liquid	-106.00 ¹⁴	-112.47	6.47
 Isopropyl nitrate	Liquid	-54.90 ¹⁴	-70.84	15.94
2, 2-Dinitropropane	Solid	-44.87 ¹⁴	-41.37	-3.50
Trinitromethane	Solid	-11.50 ¹⁴	-21.59	10.09
 2-Methyl-3-(nitrooxy)-2-[(nitrooxy)methyl]propyl nitrate	Liquid	-106.0 ¹⁴	-112.47	6.47
 <i>N,N</i> -Bis(2,2-dinitropropyl)- <i>N</i> -nitroamine	Solid	-55.4 ¹⁴	-49.76	-5.64
 1,1,1,3,5,5,5-Heptanitropentane	Solid	-36.7 ¹⁴	-42.75	6.05
 <i>N'</i> -Nitroguanidine	Solid	5.28±0.19 ¹⁷	11.30	-6.02
<i>AROMATIC COMPOUNDS</i>				
2-Ethylnitrobenzene	Liquid	-11.6±1.5 ¹⁷	-10.30	-1.30
4-Ethylnitrobenzene	Liquid	-13.2±1.5 ¹⁷	-10.30	-2.90
1-Nitronaphthalene	Solid	10.2±1.2 ¹⁷	20.47	-10.27
1, 5-Dinitronaphthalene	Solid	7.3±1.1 ¹⁷	12.72	-5.42

Molecule	State	Experimental ΔH_f (kcal/mole)	Theoretical ΔH_f (kcal/mole)	Error (kcal/mole)
 3-Nitro-1,1'-biphenyl	Solid	15.6±1.5 ¹⁷	20.78	-5.18
2-Nitroaniline	Solid	-6.29±0.77 ¹⁷	-6.33	0.04
2, 4-Dinitrotoluene	Solid	-17.10±0.65 ¹⁷	-16.99	-0.11
2, 6-Dinitrotoluene	Solid	-12.22±0.86 ¹⁷	-16.99	4.77
2, 4-Dinitro-m-xylene	Solid	-20.5±1.0 ¹⁷	-24.89	4.39
1, 3-Dinitroethylbenzene	Liquid	-21.3±1.0 ¹⁷	-22.07	0.77
 N-Methyl-N-(2,4,6-trinitrophenyl)amine	Solid	-11.90±0.86 ¹⁷	-17.09	5.19
 3-Methyl-2,4,6-trinitrophenol	Solid	-61.16±0.55 ¹⁷	-75.49	13.89
1, 3, 5-Trinitrotoluene	Solid	-10.45±0.45 ¹⁷	-16.77	6.32
2, 4, 6-Trinitrotoluene (TNT)	Solid	-16.03±0.65 ¹⁷	-24.62	8.32
2, 4, 6-Trinitrophenol(Picric acid)	Solid	-51.23±0.33 ¹⁷	-67.68	16.45
2, 3-Dinitroaniline	Solid	-2.8±0.7 ¹⁷	-6.14	3.34
2, 5-Dinitroaniline	Solid	-10.6±0.7 ¹⁷	-14.14	3.54
2, 6-Dinitroaniline	Solid	-12.1±0.7 ¹⁷	-14.14	2.04
1, 3, 5-Triamino-2,4,6-trinitrobenzene (TATB)	Solid	-33.4 ¹⁸	-31.37	-2.03
3, 4-Dinitroaniline	Solid	-7.80 ¹⁷	-14.14	6.34
1, 3, 5-Trichloro-2,4,6-trinitrobenzene (TCTNB)	Solid	Not available	-37.57	
<i>ALIPHATIC RING COMPOUNDS</i>				
RDX	Solid	15.9 ¹⁴	18.63	-2.73
HMX	Solid	21.0 ¹⁴	23.39	-2.39
 1,4-Dinitropiperazine	Solid	-12.7 ¹⁴	0.83	-13.53
 1,3,5-Tetranitrohexahydropyrimidine	Solid	2.0 ¹⁴	0.09	1.91

Molecule	State	Experimental ΔH_f (kcal/mole)	Theoretical ΔH_f (kcal/mole)	Error (kcal/mole)
 <p>1,3,3,5,7,7-Hexanitro-1,5-diazocane</p>	Solid	-5 ¹⁴	-13.13	8.13
 <p>Octanitrocubane</p>	Solid	76.6 ¹⁹ (QSPR)	72.43	-
 <p>1,1,3,3,5,5,7,7-Octanitrocyclooctane</p>	Solid	-45.3 ¹⁹ (QSPR)	-49.37	-
 <p>2,2,4,4,5,5-Hexanitrobicyclo[1.1.1]pentane</p>	Solid	Not available	-12.85	-
 <p>2,4,6,8,10,12-Hexanitrohexaazaisowurtzitane (CL20)</p>	Solid	99 ¹⁴ (Predicted)	85.04	-
 <p>1,3,3-Trinitroazetidine (TNAZ)</p>	Solid	3.7 ²⁰	-4.63	8.33

The Bourasseau procedure remains to be tested for molecules containing alcoholic groups, whereas the current procedure gives very good results for the aforesaid molecules.

5. CONCLUSION

A fairly simple procedure based on the group additivity methods along with certain thermodynamic correlations, has been described in this paper. Even though precise quantum mechanical calculations provide highly accurate results, but their usage is rather limited to relatively simple molecules because of intensive computations. The present method provides quick and sufficiently accurate values. Based on the results obtained, the method seems to be a reliable and efficient tool for prediction of heat of formation. The method may also be used to get a preliminary idea of heat of formation/reaction before proceeding towards actual experimental determination of heat of formation/reaction. The procedure may be employed for pre-synthesis thermodynamic, and certain ballistic property evaluation of target molecules.

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