



Prediction of the Condensed Phase Enthalpy of Formation of Nitroaromatic Compounds Using the Estimated Gas Phase Enthalpies of Formation by the PM3 and B3LYP Methods

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Abstract: A new method is introduced to correlate the condensed phase enthalpies of formation of nitroaromatic compounds with their gas phase enthalpies of formation on the basis of the B3LYP/6-31G* and PM3 methods. For the B3LYP method, the condensed phase enthalpy of formation depends on the number of certain elements, nitro groups and aromatic rings. For the PM3 method the number of N=N or N≡N groups, and the presence or absence of three interconnected rings, in addition to some of the parameters mentioned above, are necessary in order to obtain a reliable correlation. For 72 nitroaromatic compounds, the calculated root mean square (rms) deviations of the condensed phase enthalpies of formation of nitroaromatic compounds using the B3LYP and PM3 methods are 63.63 and 32.17 kJ/mol, respectively. The results predicted on the basis of the PM3 method are compared with the best available experimental data.

Keywords: condensed phase enthalpy of formation, gas phase enthalpy of formation, nitroaromatic compounds, PM3, B3LYP

1 Introduction

Energetic materials can be decomposed, ignited or exploded as a result of external stimuli. In order to investigate the thermodynamic stability and performance of

these materials, a knowledge of the condensed phase enthalpy of formation is an essential requirement. The experimental methods available for determining the properties of energetic materials are limited, so computational methods can be used in these cases. Among the proposed methods, quantum mechanical methods, group additivity methods and empirical methods are suitable for prediction of the enthalpy of formation of energetic materials [1-3].

Quantum mechanical methods can be used to calculate desirable molecular properties. Semi-empirical quantum mechanical methods such as MNDO, PM3 and AM1 can be helpful for prediction of the gas phase enthalpy of formation of energetic materials. For example, Chen *et al.* [4] calculated the heats of formation and molecular structures of nitrobenzenes, nitrotoluenes, nitroanilines, and nitrophenols by the AM1 and PM3 methods. The correlation between these theoretically calculated enthalpies of formation and experimental results was usually evaluated using the multivariate linear regression method. Luis *et al.* [5] have used the PM3 and AM1 methods to obtain the gas phase enthalpy of formation of nitro compounds. They showed that the PM3 method can provide better performance than the AM1 method. Akutsu *et al.* [3] combined the predicted enthalpies of vaporization and sublimation with gas phase enthalpies of formation calculated by the PM3 and MM2 methods in order to calculate the condensed phase enthalpies of formation of some energetic compounds. The DFT method can also be usefully used for prediction of enthalpies of formation. For example, Rice *et al.* [6] combined the gas phase enthalpy of formation with the evaporation and sublimation enthalpies, based on Hess's law, in order to obtain the condensed phase heats of formation of energetic compounds. Rice also predicted the heats of sublimation and vaporization from information obtained from the quantum-mechanically calculated electrostatic potential of each isolated CHNO molecule, evaluated by semi-empirical computational methods [7]. A B3PW91/6-31G** computational procedure has been presented for predicting standard gas phase heats of formation based on the estimation of the heats of vaporization and sublimation via the calculated electrostatic potential on the molecular surface [8, 9]. These authors also used the surface electrostatic potential of single molecules advised by Politzer *et al.* [10-12] for determining the enthalpies of sublimation and evaporation.

The group additivity method assumes that the molecular properties can be determined via the atoms, the functional groups and the molecular fragments in the molecule. The additivity methods of Benson, Yoneda and Joback [13] are the three usual procedures for estimating the ideal gas phase enthalpies of formation for many classes of organic compounds. For example, Joback's method [13] proposed a simple method in which the ideal gas phase heat of formation of an organic compound can be found by addition of the values of the gas phase

enthalpies of formation of groups such as $-\text{CH}_3$ and $-\text{OH}$ [13]. Salmon and Dalmazon [14] suggested a group additivity method for the estimation of the solid phase enthalpy of formation at 298.15 K of organic compounds, which can be used for energetic compounds containing $-\text{NO}_2$, $-\text{O}-\text{NO}_2$ and $-\text{N}-\text{NO}_2$ groups.

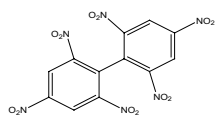
For estimation of the solid phase enthalpy of formation of energetic compounds at 298.15 K, a suitable empirical method has been introduced to predict their enthalpies of sublimation [15], which can then be combined with the gas phase enthalpy of formation of energetic compounds. It was recently indicated that the elemental composition and several specific molecular moieties can be used to predict the condensed phase enthalpy of formation of some classes of energetic compounds [16, 17]. The results showed that the condensed phase enthalpy of formation depends on decreasing or increasing energy content parameters. Because of their high intermolecular interactions, strong polar groups can enhance thermodynamic stability, and so the distribution of these groups is important in decreasing the energy of these compounds. The purpose of this work is to correlate the calculated gas phase enthalpy of formation of different nitroaromatic compounds, using the B3LYP/6-31G* and PM3 methods, with their condensed phase enthalpy of formation. It will be shown that there is no need to use evaporation and sublimation enthalpies. Finally, the predicted results will be compared with the best available experimental data.

2 Computational Method

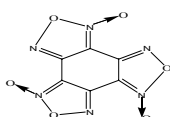
In this work, the gas phase enthalpies of formation for the selected nitroaromatic compounds (Figure 1) have been calculated by both the B3LYP/6-31G* and PM3 methods, assisted by Gaussian 03 [18] (Table 1). In both methods, the optimized molecules were certified by the absence of imaginary frequencies. The gas phase enthalpies of formation at the B3LYP level of theory are calculated by the following equation:

$$\Delta H_f(g) = E - \sum_j n_j \varepsilon_j \quad (1)$$

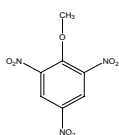
where E and n_j are the internal energy of the molecule and the number j of atoms in the molecule, respectively, and ε_j is the correction factor for the j^{th} atom at the used level of theory presented by Rice [6]. $\Delta H_f(g)$ is directly evaluated from the Gaussian output files at the PM3 level of theory. Then, the output results for the enthalpy of formation are converted to the condensed phase enthalpy of formation using multivariate linear regression relationships.



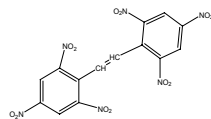
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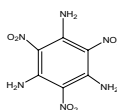
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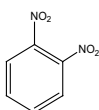
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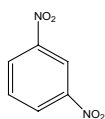
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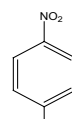
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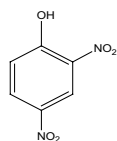
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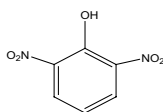
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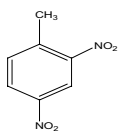
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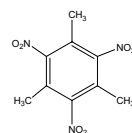
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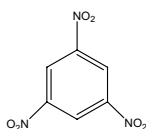
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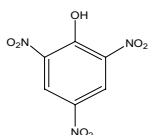
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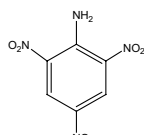
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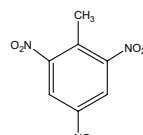
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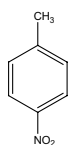
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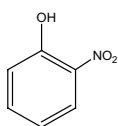
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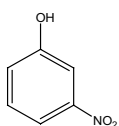
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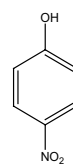
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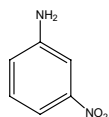
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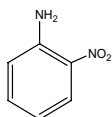
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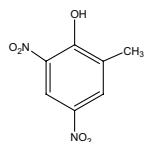
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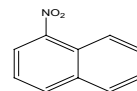
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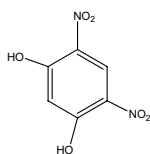
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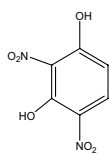
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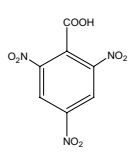
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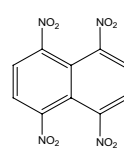
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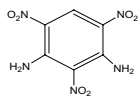
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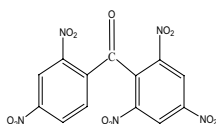
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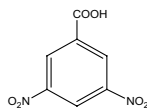
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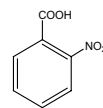
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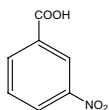
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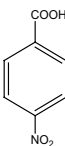
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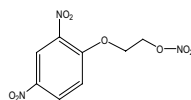
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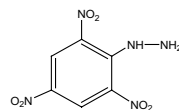
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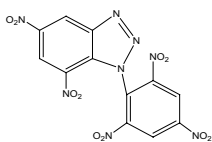
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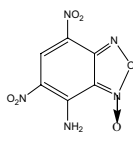
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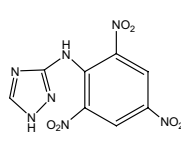
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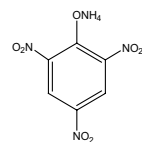
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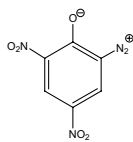
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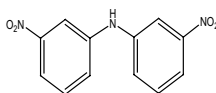
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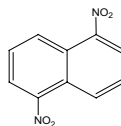
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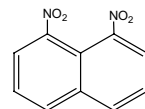
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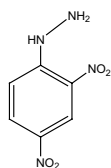
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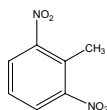
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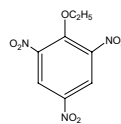
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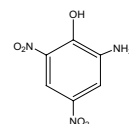
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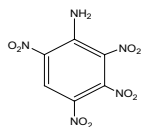
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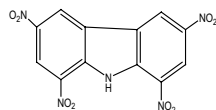
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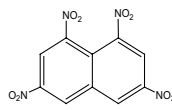
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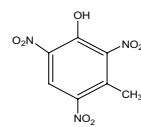
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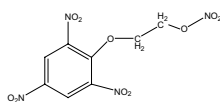
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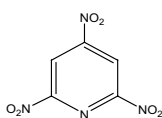
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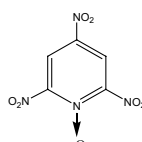
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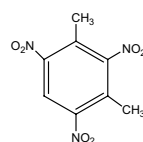
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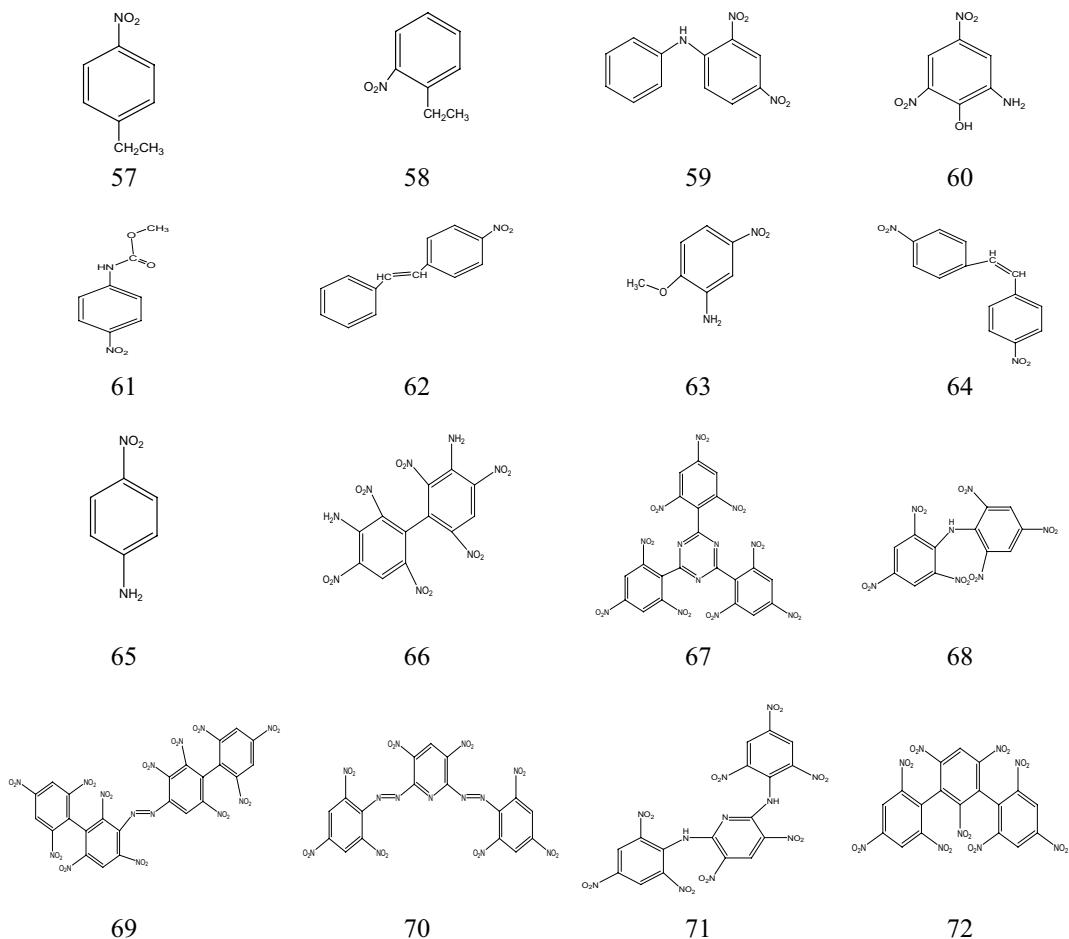


Figure 1. The structures of the selected nitroaromatic compounds.

Table 1. The calculated gas phase enthalpies of formation (in kJ/mol) for the selected molecules using: a) B3LYP/6-31G*, and b) PM3 methods

No.	$\Delta H_f(g)^a$	$\Delta H_f(g)^b$	No.	$\Delta H_f(g)^a$	$\Delta H_f(g)^b$	No.	$\Delta H_f(g)^a$	$\Delta H_f(g)^b$
1	71.691	142.54	25	-317.443	-375.16	49	91.473	52.16
2	700.638	832.34	26	-233.806	-337.78	50	102.714	105.42
3	-71.337	-108.26	27	-258.712	-296.16	51	434.086	129.52
4	238.438	184.33	28	183.254	158.77	52	-118.621	-178.66
5	30.084	-45.18	29	13.219	-27.87	53	-166.061	-201.83
6	73.809	62.61	30	37.578	31.40	54	101.256	81.66
7	29.762	37.49	31	-305.400	-324.53	55	178.019	69.55
8	29.022	41.32	32	-258.591	-289.61	56	1.193	-5.108
9	-143.198	-168.99	33	-293.308	-308.24	57	-3.204	-0.58
10	-111.408	-156.42	34	-291.808	-305.73	58	7.329	15.34
11	3.865	7.30	35	-185.362	-216.28	59	160.203	144.78
12	-11.431	-25.49	36	192.946	145.50	60	-113.748	-167.35
13	24.790	27.70	37	733.839	420.08	61	-296.667	-283.02
14	-122.761	-173.62	38	257.443	308.83	62	208.367	215.61
15	16.622	-1.80	39	264.591	277.42	63	-71.569	-102.64
16	16.640	12.86	40	10.035	-206.78	64	176.893	182.40
17	13.444	18.55	41	201.612	133.97	65	69.532	43.72
18	-118.770	-139.89	42	172.349	125.38	66	-	92.24
19	-94.524	-126.0	43	125.068	135.01	67	-	445.18
20	-100.253	-133.40	44	147.453	158.78	68	-	152.28
21	79.312	51.44	45	204.748	147.60	69	-	560.96
22	67.396	52.67	46	29.228	25.47	70	-	608.41
23	-181.036	-185.25	47	-111.103	-129.37	71	-	239.24
24	132.637	146.77	48	-69.686	-146.90	72	-	626.96

3 Results and Discussion

For the B3LYP/6-31G* and PM3 methods, it was found that several molecular moieties are essential for deriving suitable correlations between the condensed and gas phase enthalpies of formation of nitroaromatic compounds. Experimental data for the condensed phase enthalpies of formation for 72 different nitroaromatic compounds are given in Table 2. These were used to find additional correcting structural parameters through a multiple linear regression method [19]. Since the equation set is overdetermined, the left-division method for solving linear equations uses the least squares method [19] for both the B3LYP/6-31G* and PM3 methods. Various structural parameters have been examined and optimized

with the experimental data. It was found that the number of nitro groups (n_{NO_2}) and aromatic rings (n_{Ar}) as well as the number of carbon (n_C), oxygen (n_O) and hydrogen atoms (n_H) are effective parameters for the B3LYP/6-31G* method. The correlation can be given as follows:

$$\Delta_f H^\circ(C) = 0.874[\Delta_f H^\circ(g)]_{B3LYP/6-31G^*} + 35.575n_C - 31.947n_O + 30.5n_{NO_2} - 22.59n_H - 141.91n_{Ar} \quad (2)$$

where $\Delta_f H^\circ(C)$ and $[\Delta_f H^\circ(g)]_{B3LYP/6-31G^*}$ are the condensed and gas phase enthalpies of formation, Eq. (1), of nitroaromatic compounds in kJ/mol, respectively. The R-squared value or the coefficient of determination of Eq. (2) is relatively good, and equal to 0.914. The root mean square (rms) deviation of $\Delta_f H^\circ(C)$ calculated through Eq. (2) with respect to the experimental data is 62.7 kJ/mol.

The condensed phase enthalpies of formation were also determined by using the resultant values of the gas phase enthalpy of formation by PM3. Many attempts were made to obtain the minimum deviation from the experimental enthalpy of formation by means of additional effective molecular structural moieties, beside several of the previous parameters. The best correlation can be given as follows:

$$\Delta_f H^\circ(C) = 0.911[\Delta_f H^\circ(g)]_{PM3} + 26.968n_O - 10.8n_H + 46.17n_{NO_2} - 101.14n_{N_2} - 319.129n_{TRs} \quad (3)$$

where n_{N_2} is the number of N=N or N≡N groups, and n_{TRs} is the number of three interconnected aromatic rings. The R-squared value and the rms deviation from Eq. (3) with respect to the experimental data is 0.98 and 32.17 kJ/mol, respectively.

In order to specify the significance of the variables in Eqs. (2) and (3), the P-values for each parameter has been listed in Table 3. The reliability of Eq. (3) is higher than that of Eq. (2) because the R-squared value from Eq. (3) is higher than that from Eq. (2). Furthermore, the coefficient of the gas phase enthalpy of formation in Eq. (3) is larger than in Eq. (2), which shows that the predicted gas phase enthalpy of formation by the PM3 method is more suitable than that by the B3LYP/6-31G* method. Increasing the number of hydrogen and oxygen atoms in nitroaromatic compounds can decrease the condensed phase enthalpy of formation because the coefficients of n_O and n_H in both equations are negative. The same arguments can be applied for the coefficients of the other variables of Eqs. (2) and (3) in order to specify the relative contributions of the different parameters.

Table 2. The experimental condensed phase enthalpies of formation [20], and the calculated condensed phase enthalpies of formation (in kJ/mol) for the selected molecules using: a) B3LYP/6-31G*, b) PM3, c) Keshavarz, d) Salamon-Dalmazan, and e) Rice methods

No.	$\Delta H_f(\text{C})(\text{exp})$	$\Delta H_f(\text{C})^a$	$\Delta H_f(\text{C})^b$	$\Delta H_f(\text{C})^c$	$\Delta H_f(\text{C})^d$	$\Delta H_f(\text{C})^e$	Dev ^a	Dev ^b	Dev ^c	Dev ^d	Dev ^e
1	68.2	-84.96	40.15	49.7	27.3	-	153.16	28.04	18.5	40.9	-
2	606.3	492.21	596.5	585.8	627.6	-	114.08	9.8	20.4	-21.3	-
3	-187.2	-200.31	-202.84	-194.2	-174.2	-183.92	13.11	15.63	7.0	-13.0	-3.28
4	67.8	86.73	56.62	87.9	78.2	-39.71	-18.93	11.17	-20.1	-104	107.51
5	-74.7	-137.89	-129.21	-95.6	-128.8	-86.94	63.19	54.51	20.9	54.1	12.24
6	-1.7	-21.01	-1.65	-34.6	-10	-12.54	19.40	0.04	32.9	8.3	10.84
7	-27.2	-59.6	-24.55	-34.6	-42.8	-50.16	32.4	2.65	7.4	15.6	22.96
8	-38.5	-60.24	-21.06	-34.6	-36.8	-45.56	21.74	-17.44	-3.9	-1.7	7.06
9	-235.5	-242.71	-239.61	-247.7	-219.9	-228.65	7.21	4.11	12.2	-15.6	-6.85
10	-209.6	-214.93	-228.16	-247.7	-219.9	-199.80	5.33	18.55	38.1	10.3	-9.79
11	-66.4	-91.84	-73.68	-60.2	-69.6	-84.15	25.44	7.28	-8.2	-1.4	16.65
12	-124.5	-135.23	-143.67	-149.3	-130.8	-135.432	10.73	19.17	24.9	6.3	10.93
13	-37.2	-74.74	-30.41	-30.4	-73.5	-68.58	37.54	-6.78	-6.9	36.3	31.35
14	-217.9	-235.64	-240.78	-243.5	-250.7	-226.55	17.74	22.88	25.6	32.8	-21.84
15	-72.8	-104.47	-68.09	-52.1	-92.0	-89.03	31.67	-4.71	-20.7	19.2	16.23
16	-63.2	-91.47	-65.53	-56.0	-92.6	-87.36	28.27	2.33	-7.1	29.4	24.16
17	-48.2	-72.68	-66.44	-64.4	-46.5	-66.46	24.48	18.24	16.2	-1.7	18.26
18	-204.6	-210.57	-216.14	-188.0	-189.2	-189.77	5.97	-14.83	-16.6	-15.4	-14.83
19	-205.7	-189.38	-203.49	-188.0	-209.0	-193.12	-16.32	-12.58	-17.6	3.3	-12.58
20	-207.1	-194.38	-210.24	-188.0	-209.0	-208.16	-12.71	1.06	-19.1	1.9	1.06
21	-36.4	-28.09	-25.68	-60.5	-22.1	-26.33	-8.30	-10.16	24.1	-14.3	-10.16
22	-26.4	-38.50	-24.57	-60.5	-26.2	-32.18	12.10	5.68	34.1	-0.2	5.68

No.	$\Delta H_f(C)(\text{exp})$	$\Delta H_f(C)^a$	$\Delta H_f(C)^b$	$\Delta H_f(C)^c$	$\Delta H_f(C)^d$	$\Delta H_f(C)^e$	Dev ^a	Dev ^b	Dev ^c	Dev ^d	Dev ^e
23	-279.1	-285.39	-276.03	-273.4	-254.4	-269.85	6.29	-9.91	-5.7	-24.7	-9.91
24	45.7	-3.69	50.36	43.1	43.0	-	49.39	4.66	2.7	2.7	-
25	-443.4	-426.95	-454.39	-460.8	-416.8	-	-16.45	10.99	17.4	26.6	-
26	-422.6	-353.85	-420.34	-460.8	-416.8	-	-68.74	-2.26	38.3	5.8	-
27	-409.7	-350.84	-379.37	-424.3	-466.3	-	-58.86	-30.32	14.7	56.7	-
28	47.3	8.16	70.44	55.7	47.8	-	39.13	-23.14	-8.4	-0.5	-
29	-97.9	-130.04	-102.64	-73.8	-110.3	-	32.14	4.74	-24.1	12.4	-
30	-114.6	-100.36	-91.10	-135.3	-114.3	-	30.34	0.25	20.6	0.3	-
31	-432.6	-380.85	-408.26	-428.5	-455.5	-	-15.01	-27.78	-4.1	22.9	-
32	-398.7	-329.14	-379.51	-432.7	-408.1	-	-69.55	-19.19	34.0	9.4	-
33	-413.8	-359.49	-396.48	-432.7	-427.9	-	-54.31	-17.32	18.9	14.1	-
34	-427.2	-358.17	-394.18	-432.7	-427.9	-	-69.02	-33.01	5.5	0.7	-
35	-298.8	-341.53	-349.8	-273.2	-287.2	-	42.73	51.0	-25.6	-11.6	-
36	36.5	27.04	55.30	0.8	15.9	-	9.45	-18.8	35.7	20.6	-
37	300.0	527.14	300.74	330.7	297.4	-	-227.14	-0.74	-30.7	2.6	-
38	86.3	98.09	225.70	-	-	-	98.09	-139.4	-	-	-
39	151.5	160.81	175.48	175.6	152.5	-	-9.30	-23.98	24.2	1.0	-
40	-386.4	-187.36	-303.38	-	-	-	-199.03	-83.01	-	-	-
41	194.0	103.84	159.13	-	-	-	90.16	34.86	-	-	-
42	22.9	23.59	1.52	11.2	38.0	-	-0.69	21.37	11.6	-15.1	-
43	30.6	-21.09	42.69	47.3	12.2	-	51.69	-12.09	-16.7	18.4	-
44	37.6	-1.53	64.34	47.3	60.8	-	39.13	-26.74	-9.6	-23.2	-
45	50.0	48.15	54.16	7.3	46.7	-	1.84	-4.16	42.7	3.3	-
46	-55.2	-69.67	-57.09	-60.2	-61.9	-84.15	14.47	1.89	5.0	6.7	28.95
47	-200.8	-244.68	-243.67	-240.8	-196.7	-	43.88	42.87	40.1	-4.1	-

No.	$\Delta H_f(C)(\text{exp})$	$\Delta H_f(C)^a$	$\Delta H_f(C)^b$	$\Delta H_f(C)^c$	$\Delta H_f(C)^d$	$\Delta H_f(C)^e$	Dev^a	Dev^b	Dev^c	Dev^d	Dev^e
48	-248.1	-201.06	-230.29	-269.4	-229.9	-	-47.04	-17.81	21.3	-18.2	-
49	-48.9	-49.84	-15.88	-47.9	-63.9	-	0.94	-33.02	-1.0	15.0	-
50	18.9	-13.67	11.04	67.1	3.2	-	32.56	7.85	-48.2	15.7	-
51	10.8	227.39	43.79	55.7	-49.2	-	-216.39	-32.99	-44.8	60.0	-
52	-252.1	-241.64	-266.97	-269.2	-269.8	-	-10.46	14.87	17.0	17.7	-
53	-277.3	-335.45	-333.58	-296.0	-286.6	-	58.15	56.28	-8.3	9.3	-
54	78.8	-20.89	29.54	69.2	-13.0	-	99.68	49.25	9.6	91.8	-
56	-102.5	-114.59	-103.5	-102.7	-111.7	-	12.08	1.0	0.2	9.2	-
57	-55.5	-96.84	-105.48	-48.1	-47.1	-	41.54	50.14	-7.3	-8.2	-
58	-48.7	-87.63	-90.97	-48.1	-39.4	-	38.93	42.27	-0.6	-9.3	-
59	22.5	12.97	19.19	11.2	38.0	-	9.52	3.30	11.3	-15.5	-
60	-246.6	-209.06	-248.92	-	-	-	-37.53	2.32	-	-	-
61	-427.9	-394.63	-405.91	-426.4	-411.3	-	-33.26	-21.99	-1.5	-16.6	-
62	102.7	114.42	69.87	66.9	115.9	-	-11.72	32.83	35.8	13.2	-
63	-232.0	-201.52	-214.61	-224.3	-185.5	-	-30.47	-17.38	-7.7	-46.5	-
64	74.1	76.12	42.66	71.1	85.1	-	-2.02	31.43	3.0	-11.0	-
65	-45.6	-36.64	-32.71	-65.5	-22.1	-	-8.95	-12.88	-14.9	-23.5	-
66	-15.1	-	-27.27	6.3	-9.5	-	-	12.17	-21.3	-5.6	-
67	-296.6	-	-271.01	-296.0	-322.6	-	-	25.58	0.6	-26.0	-
68	44.6	-	38.32	-	-	-	-	6.28	-	-	-
69	480.3	-	454.37	478.8	494.2	-	-	25.92	1.6	-13.9	-
70	617.1	-	640.53	664.7	649.9	-	-	-23.43	-47.5	-32.8	-
71	80.3	-	80.35	83.6	-24.7	-	-	-0.05	-3.2	105.0	-
72	132.2	-	128.28	129.8	125.4	-	-	3.91	2.4	6.8	-

As indicated in Table 2, the predicted results from Eq. (3) were compared with those from the Keshavarz [17], Salamon-Dalmazon [14] and Rice *et al.* [6] methods. For those molecules where the Keshavarz [17] and Salamon-Dalmazon [14] methods can be applied, the rms deviations of the predicted condensed phase enthalpies of formation are 22.77, 26.81 and 22.23 kJ/mol from Eq. (3), the Keshavarz method [14] and the Salamon-Dalmazon method [14], respectively. Meanwhile, the rms deviations from Eq. (3) and from the Rice *et al.* [6] method are 16.01 and 27.52 kJ/mol, respectively, for those compounds where the computed values from the Rice *et al.* [6] method were reported. Thus, the reliability of Eq. (3) is close to the method of Salamon-Dalmazon [14] and better than both the Keshavarz [17] and Rice *et al.* [6] methods.

Table 3. Coefficient P-values for Eqs. (1) and (2)

P-values			
Eq. (1)		Eq. (2)	
$[\Delta_f H^\circ(g)]_{B3LYP/6-31G^*}$	5.73×10^{-25}	$[\Delta_f H^\circ(g)]_{PM3}$	1.55×10^{-50}
n_C	5.11×10^{-3}	n_O	1.61×10^{-9}
n_O	3.93×10^{-4}	n_H	7.34×10^{-13}
n_{NO_2}	7.31×10^{-3}	n_{NO_2}	2.54×10^{-7}
n_H	8.24×10^{-4}	n_{N_2}	2.41×10^{-8}
n_{Ar}	1.07×10^{-2}	n_{TRs}	1.72×10^{-12}

4 Conclusion

Two different correlations on the basis of the B3LYP/6-31G* and PM3 methods were introduced to calculate the condensed phase enthalpies of formation of nitroaromatic energetic compounds. It has been shown that Eq. (3), which is based on the PM3 method, gives more reliable results than Eq. (2). Since the gas phase enthalpy of formation of the different nitroaromatic compounds can be easily evaluated by the PM3 method, Eq. (3) can provide a simpler reliable route for calculating the condensed phase enthalpies of formation of nitroaromatic compounds, compared to the complex quantum mechanical method of Rice *et al.* [6]. Furthermore, the methods of Salamon-Dalmazon [14] and Keshavarz [17] may give larger deviations for nitroaromatic compounds with complex molecular structures, as compared to the present method.

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