Theor Chem Acc (2005) 113: 35–41
DOI 10.1007/s00214-004-0609-9

Theoretical
Chemistry Accounts

Regular article

Polyparametric modification equation for estimating thermodynamic properties of energetic nitro compounds

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Received: 22 October 2003 / Accepted: 21 May 2004 / Published online: 6 December 2004

Abstract. Calculation methods, based on hybrid density-functional theory with the basis sets of B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d,p) and B3LYP/6-31+G(d)//B3LYP/6-31G(d,p), were applied to determine the thermodynamic characteristics of various energetic nitro compounds. A parametric modification equation and the least-squares approach were used to identify 21 of the energetic research compounds. The atomization energies of these 21 compounds have an average relative error of 0.21–0.25% of the experimental values. The enthalpy (ΔH_f) and the Gibbs energy (ΔG_f) of formation have mean absolute errors of 10.8–11.4 kJ/mol (2.6–2.7 kcal/mol) and 10.0–10.3 kJ/mol (2.4 kcal/mol), respectively. The enthalpy and the Gibbs energy of formation obtained exceed those in the literature obtained by semiempirical calculations. The calibrated least-squares parameters and parametric equations were used to predict ΔH_f and ΔG_f for the five newly developed energetic nitro compounds for further applications.

Keywords: Hybrid density-functional theory – Thermodynamic properties – Energetic nitro compounds – Least-squares estimation

1 Introduction

The thermodynamic properties of molecules are important in engineering. In particular, the enthalpy of formation is considered to predict explosive performance, including detonation velocity and detonation pressure, whereas the Gibbs energy of formation is applied to estimate the reaction spontaneity [1]. Detailed thermodynamic data on most explosive compounds are either unknown or unpublished [2]. Obtaining accurate data to support applications has recently become an important issue. Reducing the absolute errors from their experimental values is a primary motivation for quantum chemical calculations [3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15]. Theoretical calculation methods and a least-squares approach have been used to derive a three-parametric modification equation, that involves C, H and a constant, and to calculate ΔH_f and ΔG_f for aliphatic C_1–C_{16} alkanes [16, 17]. The computations reveal that the error in the calculation of the enthalpy of formation in the authors' previous study was about 1.8 kJ/mol, which was better than 2.3 kJ/mol, i.e., the error in the G3(MP2)//B3LYP calculation by Redfern et al. [9].

This work considered 26 nitro compounds; a five-parametric modification equation was generated to calculate their related thermodynamic energies. The most explosive and propellant compounds contain C, H, O and N atoms, so this work addressed modifications to the atomic energies of the C, H, O and N atoms and the influence of the different atomic numbers on the calculated related energies. In a manner related to the concept of the size-consistency that relative errors in a calculation should increase more or less in proportion to the size of the molecule. A molecule with many atoms requires better correction than one with a few atoms to yield reasonable results for computational energy.

2 Calculations

2.1 Self-consistent-field optimized geometry

This study chose a B3LYP [18, 19] model derived from hybrid density-functional theory (DFT) and applied the 6-31G(d,p) basis set to predict the optimized molecular

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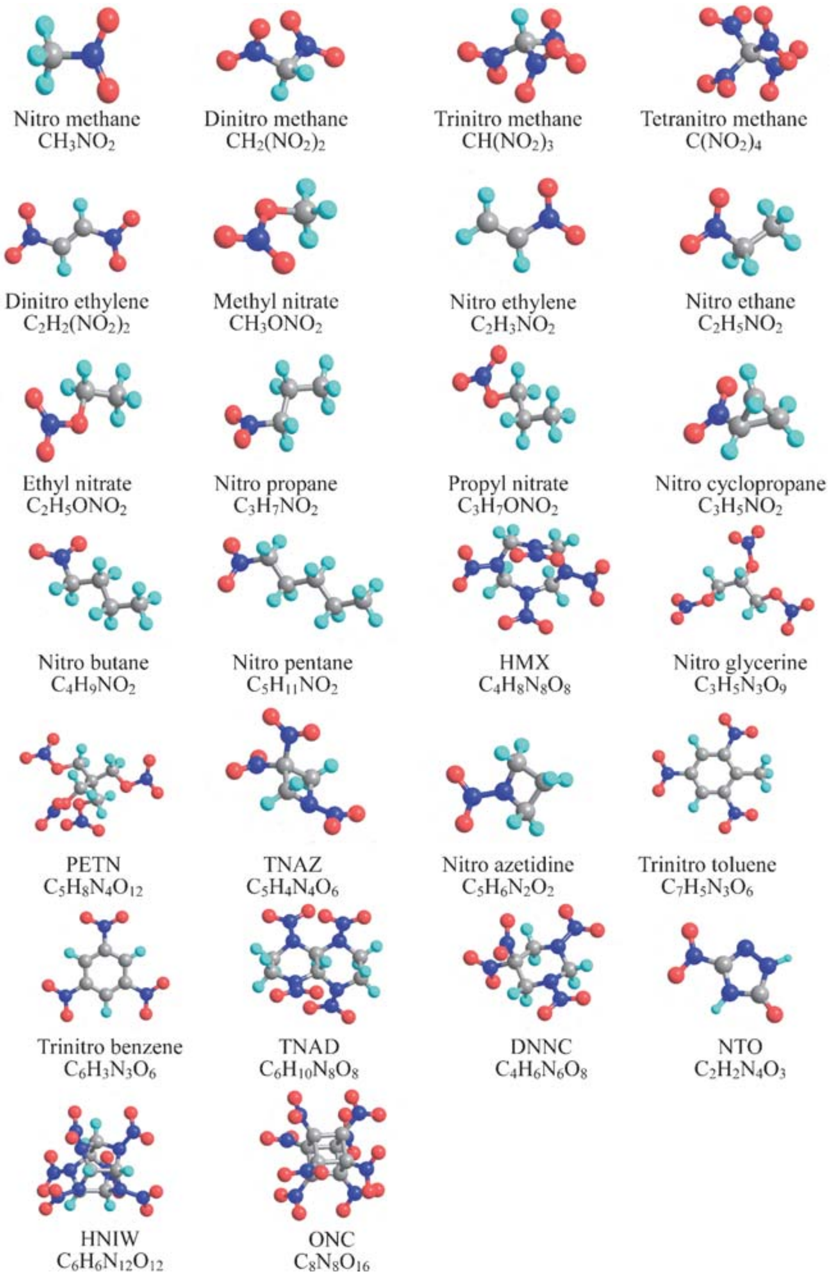
Fig. 1 Twenty six energetic nitro compounds



geometry with the help of the Gaussian 98 software [20]. All vibration frequencies are real and positive and all molecules at the local minima are stable. The thermal corrections to the enthalpy and Gibbs energy data were made manually.

2.2 Molecular thermodynamic energies

The B3LYP/6-311 + G(2d,p) and B3LYP/6-31 + G(d) methods were used to calculate the single-point molecular energy and the C, H, O and N atomic energies. Molecular thermal enthalpy and Gibbs energy were obtained by adding thermal correction to the molecular energy.

2.3 Least-squares approach to calibrating ΔH_f and ΔG_f

This first part of the calculation first determines the heat of atomization ($\Delta H_{\mathrm{a,cal}}$ and $\Delta G_{\mathrm{a,cal}}$) of a specific $C_{n_C}H_{n_H}N_{n_N}O_{n_O}$ molecule (Eq. 1) from DFT data. A five-parametric equation was established as an auxiliary equation to calibrate the least-squares heat of atomization ($\Delta H_{\mathrm{a,ls}}$ and $\Delta G_{\mathrm{a,ls}}$). All energy values are compared with the experimental energies of atomization ($\Delta H_{\mathrm{a,obs}}$ and $\Delta G_{\mathrm{a,obs}}$) and experimental values are finally used to yield the enthalpy ($\Delta H_{\mathrm{f,ls}}$) and Gibbs energy of formation ($\Delta G_{\mathrm{f,ls}}$) of the target molecule (Eqs. 2, 3):

Table 1. Comparison of the thermal enthalpy of atomization of nitro compounds at 298 K

Compound	Energy			
	H_{cal}	$\Delta H_{\mathrm{a,obs}}{}^{\mathrm{c}}$	$\Delta H_{\mathrm{a,cal}}$ (RE)	$\Delta H_{\mathrm{a,ls}}$ (RE)
CH_3NO_2	−245.042973[a]	2,422.43	2,401.67 (−0.86%)	2,416.14 (−0.26%)
	−244.969466[b]		2,391.44 (−1.28%)	2,417.12 (−0.22%)
$CH_2(NO_2)_2$	−449.585537	3,156.33	3,106.87 (−1.57%)	3,142.63 (−0.43%)
	−449.452065		3,086.16 (−2.22%)	3,143.19 (−0.42%)
$CH(NO_2)_3$	−654.118176	3,861.34	3,786.02 (−1.95%)	3,843.06 (−0.47%)
	−653.924255		3,753.55 (−2.79%)	3,841.93 (−0.50%)
$C(NO_2)_4$	−858.637352	4,518.70	4,429.82 (−1.97%)	4,508.15 (−0.23%)
	−858.383151		4,386.04 (−0.86%)	4,505.77 (−0.86%)
$C_2H_2(NO_2)_2$	−487.676522	3,752.08	3,726.24 (−0.69%)	3,770.61 (−0.49%)
	−487.534036		3,697.89 (−2.94%)	3,768.76 (0.29%)
CH_3ONO_2	−320.241576	2,712.89	2,692.85 (−0.74%)	2,713.59 (0.03%)
	−320.144888		2,680.70 (−1.19%)	2,715.57 (0.10%)
$C_2H_3NO_2$	−283.126442	3,025.08	3,001.30 (−0.79%)	3,024.38 (−0.02%)
	−283.043409		2,982.09 (−1.42%)	3,021.61 (−0.11%)
$C_2H_5NO_2$	−284.342247	3,598.07	3,568.98 (−0.81%)	3,598.04 (0.00%)
	−284.258257		3,557.14 (−1.14%)	3,598.13 (0.00%)
$C_2H_5ONO_2$	−359.542481	3,898.47	3,864.44 (−0.87%)	3,899.77 (−0.03%)
	−359.435354		3,850.80 (−1.22%)	3,900.98 (0.06%)
$C_3H_7NO_2$	−323.637097	4,771.17	4,724.67 (−0.97%)	4,768.33 (−0.06%)
	−323.542710		4,711.46 (−1.25%)	4,767.75 (−0.07%)
$C_3H_7ONO_2$	−398.837626	5,070.15	5,020.90 (−0.97%)	5,070.84 (−0.01%)
	−398.719903		5,005.37 (−1.28%)	5,070.85 (0.01%)
$C_3H_5NO_2$	−322.414579	4,193.40	4,139.37 (−1.29%)	4,177.05 (−0.39%)
	−322.323115		4,123.94 (−1.66%)	4,178.77 (−0.35%)
$C_4H_9NO_2$	−362.932515	5,943.44	5,881.85 (−1.04%)	5,940.11 (−0.06%)
	−362.827608		5,866.94 (−1.29%)	5,938.54 (−0.08%)
$C_5H_{11}NO_2$	−402.228005	7,116.56	7,039.23 (−1.09%)	7,112.08 (−0.06%)
	−402.112590		7,022.64 (−1.32%)	7109.55 (−0.10%)
HMX	−1,196.721502	10,197.79	10,014.51 (−1.80%)	10,189.54 (−0.08%)
	−1,196.380839		9,967.36 (−2.26%)	10,189.35 (−0.08%)
NG	−958.352704	7,179.84	7,099.64 (−1.12%)	7,204.69 (0.35%)
	−958.068385		7,058.52 (−1.69%)	7,205.06 (0.35%)
PETN	−1,316.690180	10,595.35	10,424.76 (−1.61%)	10,586.57 (−0.08%)
	−1,316.302407		10,369.76 (−2.13%)	10,587.44 (−0.07%)
TNAZ	−786.850437	6,279.46	6,212.91 (−1.06%)	6,307.88 (0.45%)
	−786.624518		6177.32 (−1.63%)	6,309.30 (0.48%)
$C_5H_6N_2O_2$	−377.749418	4,787.52	4,760.78 (−0.56%)	4,813.18 (0.54%)
	−377.643787		4,747.10 (−0.84%)	4,816.38 (0.60%)
TNT	−885.178788	8,995.80	8,855.73 (−1.56%)	8,976.41 (−0.22%)
	−884.932639		8,802.10 (−2.15%)	8,976.44 (−0.22%)
TNB	−845.888377	7,804.95	7,711.70 (−1.19%)	7,817.78 (0.16%)
	−845.652571		7,659.30 (−1.87%)	7,818.33 (0.17%)
Average RE	–	–	1.21%	0.21%
			1.70%	0.25%

[a] B3LYP/6-311 + G(2d,p)//B3LYP/6-31G(d,p) calculation results; H_{cal} for C is –37.855080 au, for H is –0.499795 au, for O is –75.087699 auand for N is –54.598363 au

[b] B3LYP/6-31 + G(d)//B3LYP/6-31G(d,p) calculation results; H_{cal} for C is –37.848974 au, for H is –0.497912 au, for O is –75.065246 au and for N is –54.585414 au

[c] $\Delta H_{\mathrm{f,obs}}$ for C is 716.68 kJ/mol, for H is 217.97 kJ/mol, for O is 249.20 kJ/mol and for N is 472.70 kJ/mol

* H_{cal} is in atomic units, the other values are in kilojoules per mole

Each datum in *parentheses* is the relative error as compared to experimental value

$$C_{n_C}H_{n_H}N_{n_N}O_{n_O}(g) \rightarrow n_C C(g) + n_H H(g) + n_N N(g) + n_O O(g),]] \quad (1)$$

$$\Delta H_f\left(C_{n_C}H_{n_H}N_{n_N}O_{n_O},_{gas}\right)_{ls} = n_C \Delta H_f\left(C_{gas}\right)_{obs} + n_H \Delta H_f\left(H_{gas}\right)_{obs} + n_N \Delta H_f\left(N_{gas}\right)_{obs} + n_O \Delta H_f\left(O_{gas}\right)_{obs} - \Delta H_{a,ls}, \quad (2)$$

$$\Delta G_f\left(C_{n_C}H_{n_H}N_{n_N}O_{n_O},_{gas}\right)_{ls} = n_C \Delta G_f\left(C_{gas}\right)_{obs} + n_H \Delta G_f\left(H_{gas}\right)_{obs} + n_N \Delta G_f\left(N_{gas}\right)_{obs} + n_O \Delta G_f\left(O_{gas}\right)_{obs} - \Delta G_{a,ls} \quad (3)$$

where n_C, n_H, n_N and n_O are the numbers of C, H, N and O.

Table 2. Comparison of the Gibbs energy of atomization of nitro compounds at 298 K.G_{cal} is in atomic units, the other values are inkilojoules per mole. Each datum in *parentheses* is the RE compared with the experimental value

Compound	Energy			
	G_{cal}	$\Delta G_{\mathrm{a,obs}}$[c]	$\Delta G_{\mathrm{a,cal}}$ (RE)	$\Delta G_{\mathrm{a,ls}}$ (RE)
CH_3NO_2	−245.076103[a]	2,346.19	2,199.80 (−6.24%)	2,337.59 (−0.37%)
	−245.002596[b]		2,204.33 (−6.05%)	2,338.58 (−0.32%)
$CH_2(NO_2)_2$	−449.626035	3,090.43	2,817.71 (−8.82%)	3,083.18 (−0.23%)
	−449.492563		2,833.99 (−8.30%)	3,083.74 (−0.22%)
$CH(NO_2)_3$	−654.164101	3,805.10	3,404.47 (−10.53%)	3,797.61 (−0.20%)
	−653.970180		3,431.23 (−9.83%)	3,796.47 (−0.23%)
$C(NO_2)_4$	−858.688861	4,474.91	3,956.29 (−11.59%)	4,477.10 (0.05%)
	−858.434660		3,993.98 (−10.75%)	4,474.72 (−0.01%)
$C_2H_2(NO_2)_2$	−487.717794	3,642.14	3,394.64 (−6.80%)	3,662.65 (0.56%)
	−487.575301		3,409.38 (−6.39%)	3,660.80 (0.51%)
CH_3ONO_2	−320.275515	2,642.90	2,445.40 (−7.47%)	2,634.03 (−0.34%)
	−320.178827		2,455.68 (−7.08%)	2,636.01 (−0.26%)
$C_2H_3NO_2$	−283.159856	2,899.87	2,755.72 (−4.97%)	2,896.05 (−0.13%)
	−283.076823		2,757.35 (−4.91%)	2,893.28 (−0.23%)
$C_2H_5NO_2$	−284.378001	3,476.42	3,260.66 (−6.21%)	3,478.08 (0.05%)
	−284.294011		3,262.88 (−6.14%)	3,478.17 (0.05%)
$C_2H_5ONO_2$	−359.580026	3,787.42	3,513.12 (−7.24%)	3,781.38 (−0.16%)
	−359.472899		3,521.21 (−7.03%)	3,782.58 (−0.13%)
$C_3H_7NO_2$	−323.676710	4,606.53	4,313.14 (−6.37%)	4,610.20 (0.08%)
	−323.582323		4,313.30 (−6.37%)	4,609.62 (0.07%)
$C_3H_7ONO_2$	−398.878825	4,914.85	4,565.84 (−7.10%)	4,913.73 (−0.02%)
	−398.761102		4,571.33 (−6.99%)	4,913.74 (−0.02%)
$C_3H_5NO_2$	−322.449921	4,029.08	3,785.50 (−6.05%)	4,005.47 (−0.59%)
	−322.358457		3,790.23 (−5.93%)	4,007.19 (−0.54%)
$C_4H_9NO_2$	−362.976184	5,738.71	5,367.64 (−6.47%)	5,744.33 (0.10%)
	−362.871277		5,365.39 (−6.51%)	5,742.76 (0.07%)
$C_5H_{11}NO_2$	−402.275095	6,871.36	6,420.65 (−6.56%)	6,876.98 (0.08%)
	−402.159680		6,416.04 (−6.63%)	6,874.45 (0.04%)
HMX	−1,196.787444	10,087.01	8,987.30 (−10.90%)	10,082.32 (−0.05%)
	−1,196.446781		9,026.86 (−10.51%)	10,082.13 (−0.05%)
NG	−958.413757	7,061.59	6,388.03 (−9.54%)	7,092.93 (0.44%)
	−958.129438		6,427.73 (−8.98%)	7,093.29 (0.45%)
PETN	−1,316.766805	10,434.04	9,373.01 (−10.17%)	10,415.69 (−0.18%)
	−1,316.379032		9,427.34 (−9.65%)	10,416.56 (−0.17%)
TNAZ	−786.901843	6,184.78	5,607.83 (−9.33%)	6,186.24 (0.02%)
	−786.675924		5,637.01 (−8.86%)	6,187.66 (0.05%)
$C_5H_6N_2O_2$	−377.786848	4,635.77	4,332.28 (−6.55%)	4,655.35 (0.42%)
	−377.681217		4,338.89 (−6.40%)	4,658.55 (0.49%)
TNT	−885.234865	8,676.73	8,096.29 (−6.69%)	8,658.84 (−0.21%)
	−884.988716		8,124.85 (−6.36%)	8,658.87 (−0.21%)
TNB	−845.941568	7524.83	7,058.01 (−6.20%)	7,540.94 (0.21%)
	−845.705762		7,088.51 (−5.80%)	7,541.49 (0.22%)
Average RE	–	–	7.70%	0.21%
			6.88%	0.21%

[a] B3LYP/6-311 + G(2d,p)//B3LYP/6-31G(d,p)calculation results; G_{cal} for C is –37.872017 au, for H is –0.512911 au, for O is –75.105867 auand for N is –54.615759 au

[b] B3LYP/6-31 + G(d)//B3LYP/6-31G(d,p)calculation results; G_{cal} for C is –37.863592 au, for H is –0.512320 au, for O is –75.080497 auand for N is –54.601466 au

[c] $\Delta G_{\mathrm{f,obs}}$ for C is 671.26 kJ/mol, for H is 203.25 kJ/mol, for O is 231.70 kJ/mol and for N is 455.50 kJ/mol

3 Results and discussion

This work modeled 26 nitro compounds as stable molecules with real and positive vibration frequencies (Fig. 1). Tables 1, 2, 3, 4 and 5 present the thermodynamic energies of the molecules for comparison.

3.1 Program-calculated energies

B3LYP/6-31G(d,p)-calculated thermal corrections to enthalpy and Gibbs energy were added to the B3LYP/6-311 + G(2d,p) or B3LYP/6-31 + G(d) self-consistent-field molecular energy to obtain the related H_{cal} and G_{cal} of the target molecules and their corresponding composite atoms, as shown in Tables 1 and 2. The methods used are the so-called B3LYP/6-311 + G(2d,p)//B3LYP/6-31G(d,p) and B3LYP/6-31 + G(d)//B3LYP/6-31G(d,p) methods. The atomization energies associated with the atomization reaction of a $C_{n_C}H_{n_H}N_{n_N}O_{n_O}$ molecule (Eq. 1) ($\Delta H_{\mathrm{a,cal}}$ and $\Delta G_{\mathrm{a,cal}}$) were calculated using Eqs. 4 and 5. Tables 1 and 2 compare the results. The average relative errors between the calculated and observed atomization

Table 3. Comparison of the formationenthalpy of nitro compounds at 298 K. All values are in kilojoules permole. Each datum in *parentheses* is the absolute error (*AE*) compared with the experimental value

Compound	Energy				
	$\Delta H_{\mathrm{f,obs}}$[c]	$\Delta H_{\mathrm{f,cal}}$ (AE)	$\Delta H_{\mathrm{f,ls}}$ (AE)	$\Delta H_{\mathrm{f,PM3}}$ (AE)[c]	$\Delta H_{\mathrm{f,AM1}}$ (AE)[c]
CH_3NO_2	−80.8	−60.0 (20.8)[a] −50.0 (31.0)[b]	−74.5 (6.3) −75.4 (5.3)	−66.5 (14.2)	−41.4 (39.3)
$CH_2(NO_2)_2$	−61.5	−12.1 (49.5) 8.7 (70.2)	−47.8 (13.7) −48.4 (13.1)	−49.8 (11.7)	12.1 (73.7)
$CH(NO_2)_3$	−13.4	61.9 (75.3) 94.4 (107.8)	4.9 (18.3) 6.0 (19.4)	−19.7 (−5.3)	104.6 (118.0)
$C(NO_2)_4$	82.4	171.3 (88.9) 215.0 (132.7)	92.9 (10.6) 95.3 (12.9)	26.8 (−55.6)	224.4 (142.0)
$C_2H_2(NO_2)_2$	59.4	85.3 (25.8) 113.6 (54.2)	77.9 (18.5) 76.1 (16.7)	−110.5 (−169.9)	−81.3 (−140.7)
CH_3ONO_2	−122.0	−102.0 (20.0) −89.8 (32.2)	−121.3 (0.7) −119.3 (2.7)	−135.6 (−13.6)	−131.0 (−9.0)
$C_2H_3NO_2$	33.3	57.1 (23.8) 76.3 (43.0)	34.0 (0.7) 36.8 (3.5)	30.0 (−3.3)	66.7 (33.5)
$C_2H_5NO_2$	−103.8	−74.7 (29.1) −62.9 (40.9)	−103.8 (0.0) −103.7 (0.1)	−87.5 (16.3)	−70.7 (33.1)
$C_2H_5ONO_2$	−155.0	−121.0 (34.0) −107.3 (47.7)	−153.7 (1.3) −152.5 (2.5)	−159.1 (−4.1)	−159.5 (−4.5)
$C_3H_7NO_2$	−124.3	−77.8 (46.5) −64.6 (59.7)	−121.4 (2.8) −120.9 (3.4)	−109.7 (14.6)	−99.6 (24.7)
$C_3H_7ONO_2$	−174.1	−124.8 (49.3) −109.3 (64.8)	−173.4 (0.7) −173.4 (0.7)	−178.6 (−4.7)	−185.7 (−11.6)
$C_3H_5NO_2$	17.6	71.6 (54.0) 87.0 (69.5)	33.9 (16.4) 32.2 (14.6)	–	–
$C_4H_9NO_2$	−143.9	−82.3 (61.6) −67.4 (76.5)	−140.6 (3.3) −139.0 (4.9)	−134.3 (9.6)	−127.2 (16.7)
$C_5H_{11}NO_2$	−164.4	−87.1 (77.3) −70.5 (93.9)	−160.0 (4.5) −157.4 (7.0)	−154.4 (10.0)	−148.5 (15.9)
HMX	187.9	371.1 (183.3) 418.3 (230.4)	196.1 (8.3) 196.3 (8.4)	390.7 (202.8)	732.2 (544.3)
NG	−279.1	−198.9 (80.2) −167.8 (121.3)	−254.2 (24.9) −253.9 (25.292)	−320.5 (−41.4)	−297.9 (−18.8)
PETN	−387.0	−216.4 (170.6) −161.4 (225.6)	−378.24 (8.78) −379.11 (7.91)	−410.87 (−23.9)	−398.7 (−11.7)
TNAZ	128.5	195.0 (66.6) 230.6 (102.1)	156.9 (28.4) 158.3 (29.8)	–	–
$C_5H_6N_2O_2$	114.1	140.9 (26.7) 154.5 (40.4)	139.8 (25.7) 143.0 (28.9)	–	–
TNT	24.1	164.2 (140.1) 217.8 (193.7)	43.5(19.4) 43.5(19.4)	13.8 (−10.3)	172.8 (148.7)
TNB	62.3	155.6 (93.3) 208.0 (145.7)	75.2 (12.8) 75.7 (13.4)	793.5 (731.2)	–
Mean AE	–	67.5 94.4	10.8 11.4	75.4	81.5

[a] B3LYP/6-311 + G(2d,p)//B3LYP/6-31G(d,p)calculation results

[b] B3LYP/6-31 + G(d)//B3LYP/6-31G(d,p)calculation results

[c] SeeRef. [2]

energies of the 21 nitro compounds, range from 1.21 to 7.70%.

$$\Delta H_{\mathrm{a,cal}} = n_{\mathrm{C}} H\left(\mathrm{C_{gas}}\right)_{\mathrm{cal}} + n_{\mathrm{H}} H\left(\mathrm{H_{gas}}\right)_{\mathrm{cal}} + n_{\mathrm{N}} H\left(\mathrm{N_{gas}}\right)_{\mathrm{cal}} + n_{\mathrm{O}} H\left(\mathrm{O_{gas}}\right)_{\mathrm{cal}} - H\left(\mathrm{C}_{n_{\mathrm{C}}}\mathrm{H}_{n_{\mathrm{H}}}\mathrm{N}_{n_{\mathrm{N}}}\mathrm{O}_{n_{\mathrm{O}}},\mathrm{gas}\right)_{\mathrm{cal}}, \tag{4}$$

$$\Delta G_{\mathrm{a,cal}} = n_{\mathrm{C}} G\left(\mathrm{C_{gas}}\right)_{\mathrm{cal}} + n_{\mathrm{H}} G\left(\mathrm{H_{gas}}\right)_{\mathrm{cal}} + n_{\mathrm{N}} G\left(\mathrm{N_{gas}}\right)_{\mathrm{cal}} + n_{\mathrm{O}} G\left(\mathrm{O_{gas}}\right)_{\mathrm{cal}} - G\left(\mathrm{C}_{n_{\mathrm{C}}}\mathrm{H}_{n_{\mathrm{H}}}\mathrm{N}_{n_{\mathrm{N}}}\mathrm{O}_{n_{\mathrm{O}}},\mathrm{gas}\right)_{\mathrm{cal}}. \tag{5}$$

The $\Delta H_{\mathrm{f,cal}}$ and $\Delta G_{\mathrm{f,cal}}$ were obtained by including the experimental $\Delta H_{\mathrm{f,obs}}$ and $\Delta G_{\mathrm{f,obs}}$ of C, H, O and N atoms and $\Delta H_{\mathrm{a,cal}}$ and $\Delta G_{\mathrm{a,cal}}$ of the molecules in the calculation [21]. Tables 3 and 4 reveal that the mean absolute error of the enthalpy of formation is in the range 67.5–94.4 kJ/mol and that of the Gibbs energy of formation is in the range 406.3–423.2 kJ/mol; these values are comparable to the experimental $\Delta H_{\mathrm{f,obs}}$ and $\Delta G_{\mathrm{f,obs}}$ [2].

Table 4. Comparison of the Gibbs energy of formation of nitro compounds at 298 K.All values are in kilojoules per mole. Each datum in *parentheses* is the AE compared with the experimental value

Compound	Energy		
	$\Delta G_{\mathrm{f,obs}}$[c]	$\Delta G_{\mathrm{f,cal}}$ (AE)	$\Delta G_{\mathrm{f,ls}}$ (AE)
CH_3NO_2	−146.3	0.1 (146.4)[a]	−137.7 (8.6)
		−4.4 (141.9)[b]	−138.7 (7.6)
$CH_2(NO_2)_2$	−174.9	97.8 (272.7)	−167.6 (7.3)
		81.6 (255.5)	−168.2 (6.7)
$CH(NO_2)_3$	−173.9	226.8 (400.7)	−166.4 (7.5)
		200.0 (373.9)	−165.3 (8.6)
$C(NO_2)_4$	−128.1	390.6 (518.6)	−125.9 (2.2)
		352.9 (480.9)	−127.9 (0.2)
$C_2H_2(NO_2)_2$	−55.3	192.2 (247.5)	−34.8 (20.5)
		177.4 (232.8)	−36.7 (18.7)
CH_3ONO_2	−211.3	−13.8 (197.5)	−202.4 (8.9)
		−24.1 (187.2)	−204.4 (6.9)
$C_2H_3NO_2$	−28.7	115.4 (144.2)	−24.9 (3.8)
		113.8 (142.5)	−22.1 (6.6)
$C_2H_5NO_2$	−198.8	17.0 (215.8)	−197.1 (1.7)
		14.8 (213.5)	−197.0 (1.8)
$C_2H_5ONO_2$	−278.1	−3.8 (274.3)	−272.0 (6.0)
		−11.8 (266.3)	−273.2 (4.9)
$C_3H_7NO_2$	−251.1	42.3 (293.4)	−247.5 (3.7)
		42.1 (293.2)	−248.0 (3.1)
$C_3H_7ONO_2$	−327.8	21.3 (349.0)	−326.6 (1.1)
		15.8 (343.5)	−326.6 (1.1)
$C_3H_5NO_2$	−80.2	163.4 (−243.6)	−56.6 (23.6)
		158.7 (−238.9)	−58.3 (21.9)
$C_4H_9NO_2$	−305.6	65.5 (371.1)	−299.9 (5.6)
		67.8 (373.3)	−301.5 (4.1)
$C_5H_{11}NO_2$	−360.5	90.3 (450.7)	−354.8 (5.6)
		94.9 (455.4)	−357.4 (3.1)
HMX	−278.4	821.3 (1099.7)	−273.7 (4.7)
		781.8 (1060.2)	−273.5 (4.9)
NG	−579.8	93.8 (673.6)	−548.4 (31.3)
		54.1 (633.9)	−548.1 (31.7)
PETN	−849.4	211.7 (1061.0)	−831.0 (18.4)
		157.3 (1,006.7)	−831.9 (17.5)
TNAZ	−145.8	431.1 (577.0)	−144.4 (1.5)
		402.0 (547.8)	−142.9 (2.9)
$C_5H_6N_2O_2$	−28.1	275.4 (303.5)	−8.5 (19.6)
		268.8 (296.9)	−5.4 (22.7)
TNT	−205.0	375.5 (580.5)	−187.1 (17.9)
		346.9 (551.9)	−187.1 (17.9)
TNB	−130.9	336.0 (466.8)	−114.7 (16.1)
		305.5 (436.3)	−114.2 (16.7)
Mean AE	–	423.2	10.3
		406.3	10.0

[a] B3LYP/6-311 + G(2d,p)//B3LYP/6-31G(d,p) calculation results

[b] B3LYP/6-31 + G(d)//B3LYP/6-31G(d,p) calculation results

[c] Calculated by $\Delta H_{\mathrm{f,obs}}$ and S_{obs} obtained from Ref. [2], $\Delta G_{\mathrm{f,obs}} = \Delta H_{\mathrm{f,obs}} - T\Delta S_{\mathrm{obs}}$, at 25 °C

3.2 Least-squares modified energies

$\Delta H_{\mathrm{f,cal}}$ and $\Delta G_{\mathrm{f,cal}}$ include apparent errors, and the computational results do not convince people to use them. This work aims to generate a polymetric modification equation, based on the concept of least-squares estimation, to reduce the errors related to energy values. The number of each species of atom in a specific nitro molecule that contains C, H, O and N atoms influences the calculated energies. Two five-parametric equations were created (Eqs. 6, 7), in which parameters A, B, C, D and E (or A_{g}, B_{g}, C_{g}, D_{g} and E_{g}) are modified according to the constant and the number of C, H, O and N atoms. As in the case of a satisfactory requirement for a size-consistent idea [22, 23], the effect of the computational modification will focus on molecular sizes and the number of different atoms in a nitro compound.

$$\Delta H_{\mathrm{a,ls}} = \Delta H_{\mathrm{a,cal}} + A + Bn_{\mathrm{C}_i} + Cn_{\mathrm{H}_i} + Dn_{\mathrm{N}_i} + En_{\mathrm{O}_i} \quad (6)$$

$$\begin{aligned}\Delta G_{\mathrm{a,ls}} = {} & \Delta G_{\mathrm{a,cal}} + A_{\mathrm{g}} + B_{\mathrm{g}}n_{\mathrm{C}_i} + C_{\mathrm{g}}n_{\mathrm{H}_i} + D_{\mathrm{g}}n_{\mathrm{N}_i} \\ & + E_{\mathrm{g}}n_{\mathrm{O}_i},\end{aligned} \quad (7)$$

where n_{C_i}, n_{H_i}, n_{N_i} and n_{O_i} are the number of C, H, N, O atoms of the ith molecule.

Twenty-one nitro compounds with known experimental ΔH_{f} and ΔG_{f} appearing in Tables 3 and 4 were selected for further study, so the square summation errors between the least-squares modified value of the atomization heat and the experimental values are as given in Eqs. 8 and 9:

$$\begin{aligned}\varepsilon_{\mathrm{r}_H} &= \sum_{i=1}^{21} \left(\Delta H_{\mathrm{a}_i,\mathrm{obs}} - \Delta H_{\mathrm{a}_i,\mathrm{ls}}\right)^2 \\ &= \sum_{i=1}^{21} \left(\Delta H^2_{\mathrm{a}_i,\mathrm{obs}-\Delta H_{\mathrm{a}}i,\mathrm{cal}-A-Bn_{\mathrm{C}_i}-rCn_{\mathrm{H}_i}-Dn_{\mathrm{N}_i}-En_{\mathrm{O}_i})},\end{aligned} \quad (8)$$

$$\begin{aligned}\varepsilon_{\mathrm{r}_G} &= \sum_{i=1}^{21} \left(\Delta G_{\mathrm{a}_i,\mathrm{obs}} - \Delta G_{\mathrm{a}_i,\mathrm{ls}}\right)^2 \\ &= \sum_{i=1}^{21} \Big(\Delta G_{\mathrm{a}_i,\mathrm{obs}} - \Delta G_{\mathrm{a}_i,\mathrm{cal}} - A - Bn_{\mathrm{C}_i} \\ &\quad - Cn_{\mathrm{H}_i} - Dn_{\mathrm{N}_i} - En_{\mathrm{O}_i}\Big)^2.\end{aligned} \quad (9)$$

The first derivatives of $\varepsilon_{\mathrm{r}_H}$ (or $\varepsilon_{\mathrm{r}_G}$) with respect to A, B, C, D and E (or A_{g}, B_{g}, C_{g}, D_{g} and E_{g}) are set to zero, and the simultaneous equations are solved to obtain the values of A, B, C, D and E (or A_{g}, B_{g}, C_{g}, D_{g} and E_{g}). Table 6 presents the computational results.

The least-squares modified results of $\Delta H_{\mathrm{a,ls}}$ and $\Delta G_{\mathrm{a,ls}}$, demonstrate that the average relative errors in the atomization energies are reduced to 0.21–0.25% better than those calculated directly by the program (Tables 1, 2). Additionally, $\Delta H_{\mathrm{f,ls}}$ and $\Delta G_{\mathrm{f,ls}}$ were determined from $\Delta H_{\mathrm{a,ls}}$ and $\Delta G_{\mathrm{a,ls}}$ using Eqs. 2 and 3. The mean absolute error in the enthalpy of formation is within 10.8–11.4 kJ/mol (2.6–2.7 kcal/mol) of the experimental values, substantially better than Burcat's semiempirical calculated results, $\Delta H_{\mathrm{f,PM3}} = 75.4$ kJ/mol and $\Delta H_{\mathrm{f,AM1}} = 81.5$ kJ/mol [2]. Furthermore, the mean absolute error in the Gibbs energy of formation is 10.0–10.3 kJ/mol (2.4 kcal/mol) (Tables 3, 4)

Table 5. Prediction of the enthalpy and Gibbs energy of formation of newly developed nitro compounds

Compound	Energy			
	$\Delta H_{\mathrm{f,cal}}$ (298 K)	$\Delta H_{\mathrm{f,est}}$ (298 K)	$\Delta G_{\mathrm{f,cal}}$ (298 K)	$\Delta G_{\mathrm{f,est}}$ (298 K)
TNAD	461.3[a]	263.1	947.1	−230.1
	510.8[b]	259.7	904.6	−233.4
DNNC	216.8	80.2	588.8	−300.1
	272.9	79.8	549.5	−300.4
NTO	20.2	−41.3	157.1	−189.1
	45.6	−43.5	140.0	−191.4
HNIW	764.6	506.4	1,375.7	−108.9
	839.1	499.3	1,299.8	−115.9
ONC	1,014.7	778.9	1,483.1	279.6
	1,111.9	766.9	1,380.8	267.6

[a] B3LYP/6-311 + G(2d,p)//B3LYP/6-31G(d,p) calculation results
[b] B3LYP/6-31 + G(d)//B3LYP/6-31G(d,p) calculation results

Table 6. Modification parameters of the least-squares estimation equations. *A*,*B*, *C*, *D*, and *E* are modification coefficients for each constant item, Cs, Hs, Os, Ns; The parameters with the *subscript* g are for estimating the Gibbs energy of formation

Parameter	Method	
	B3LYP/6-311 + G(2d,p)//B3LYP/6-31G(d,p)	B3LYP/6-31 + G(d)//B3LYP/6-31G(d,p)
A	−27.4012438	−22.4396809
B	8.611270227	13.83654251
C	2.992613493	0.734628812
D	6.274582536	9.182176339
E	11.73022483	13.71875159
A_{g}	−146.608938	−141.647375
B_{g}	2.538656719	1.675394498
C_{g}	38.54759322	39.68175454
D_{g}	50.83255126	46.08156156
E_{g}	64.55422476	63.01407953

3.3 A Five-parametric equation predicted energies

Table 5 lists the five-parametric equations used to estimate the ΔH_{f} and ΔG_{f} of the five newly developed energetic nitro compounds, TNAD, DNNC, NTO, HNIW and ONC [1, 24, 25, 26, 27, 28]. The predicted energies are believed to be usable as reference values because they are calculated by reliable computational procedures.

4 Conclusion

This work initially calculated the atomization heat for 21 nitro compounds using two hybrid DFT methods, B3LYP/6-311 + G(2d,p)//B3LYP/6-31G(d,p) and B3LYP/6-31 + G(d)//B3LYP/6-31G(d,p). This calculation was followed by calibrating the atomization heat using a five-parametric modification equation. The modified method yields substantially better results than the output calculated directly by the program. The average relative error between $\Delta H_{\mathrm{a,cal}}$ and $\Delta H_{\mathrm{a,ls}}$ improved from 1.70 to 0.21% and that between $\Delta G_{\mathrm{a,cal}}$ and $\Delta G_{\mathrm{a,ls}}$ from 7.70 to 0.21%. These results are sufficiently encouraging to justify further calculation work. Therefore, this study calibrated the thermodynamic characteristics of the selected 21 energetic nitro compounds, including the enthalpy and Gibbs energy of formation and then identified the mean absolute error from the experimental value. The least-squares estimates are about 10 kJ/mol and the calculated values exceed 100 kJ/mol. These calculations verify that a polyparametric modification equation derived by the least-squares method is reliable in calculating the ΔH_{f} and the ΔG_{f} of the target molecules. It can even be extended to estimate the values of unknown compounds. Therefore, this work forecasted the ΔH_{f} and ΔG_{f} of five newly developed energetic nitro compounds and provides them as a future reference.

Acknowledgements. The authors would like to thank the National Science Council of the Republic of China for financial support of this work under grant no. NSC-91-2113-M-014-003. The National Center for High-Performance Computing providing the computation facility is also acknowledged.

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