



Highly energetic nitrogen species: Reliable energetics via the correlation consistent Composite Approach (ccCA)

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ARTICLE INFO

Article history:

Received 10 August 2010
Received in revised form 6 November 2010
Accepted 9 November 2010
Available online 13 November 2010

Keywords:

Enthalpy of formation
High explosive
ccCA
Ab initio

ABSTRACT

Gas-phase enthalpies of formation ($\Delta H_{f(g)}^\circ$) have been determined for 40 nitrogen-containing compounds at 298 K. Three *ab initio* composite methods have been compared in their abilities to quantitatively determine $\Delta H_{f(g)}^\circ$; the G3, G3(MP2), and correlation consistent Composite Approach (ccCA) methodologies. The ccCA method resulted in a mean absolute deviation (MAD) of 1.1 kcal mol⁻¹ when compared to available experimental values. The comparable G3(MP2) method resulted in a MAD of 1.8 kcal mol⁻¹, while the G3 method resulted in a MAD of 1.2 kcal mol⁻¹. As a result of their comparable accuracies, the ccCA and G3 methods have been utilized to predict the $\Delta H_{f(g)}^\circ$ of five energetic but highly endothermic tetrazine-containing compounds with potential applications as insensitive high explosives.

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1. Introduction

One of the most complicated tasks that confronted the major powers during the World Wars was the development of explosives, propellants and projectiles [1]. Of the many energetic compounds developed around the time, RDX (1,3,5-trinitro-1,3,5-triazacyclohexane) has proven to be of high brisance (shattering power) but is also known to be extremely sensitive to shock, impact and friction [2]. Although RDX is still widely used for military and non-military purposes, for instance in Composition H-6 and Cyclotol explosives, it is prone to premature deflagration and detonation when employed in delayed-action payload dropped from high altitude [3]. The risks of catastrophic explosions during manufacture, storage, destruction, demilitarization and disposal of many common sensitive explosives have prompted continuing research on the discovery and synthesis of insensitive high explosives for military and commercial uses (such as fireworks, demolition, excavation, and mining) [1]. Such compounds are characterized by the swiftness with which their decomposition, detonation or explosion occur supersonically but are surprisingly insensitive to triggering stimuli such as impact, friction and electrostatic discharge. Potential alternatives to the existing shock and friction-sensitive energetic compounds include caged polynitropolycycloalkanes, polynitramines and many N-heterocycles due to their high nitrogen content. These compounds exhibit high endothermicity, a property that is suggestive of their incredible insensitivity, and high den-

sities, i.e., large amount of energy can be liberated from a small quantity of the material. These critical properties are important to explosive performance [4].

Energetic species containing nitrogen-substituted benzene rings derive their high energies from the increased carbon–nitrogen and nitrogen–nitrogen bonds, in contrast to carbon-based non-substituted explosives which draw their energies mostly from the oxidation of the carbon and hydrogen atoms [5]. The oxidation of a carbon-based explosive leads to an incomplete combustion reaction, resulting in toxic gases such as carbon monoxide and nitrogen oxides. The oxygen balance (a measurement of the ability of an explosive compound to become oxidized) of nitrogen-substituted compounds is usually close to zero, indicating a more complete combustion reaction than for carbon-based explosives. Optimal sensitivity, power, and brisance of an explosive tend to be attained as the oxygen balance approaches zero.

While highly endothermic compounds are the most sought after to ensure high insensitivity and complete decomposition [6], energetics for these mostly nitrogen-rich compounds have been observed to be directly related to explosive properties examined in propellant development. Properties derived from $\Delta H_{f(g)}^\circ$ include: enthalpy of explosion (ΔH_e) which is used in computing the temperature of explosion (T_e), work potential (nRT), and velocity of detonation (VOD) which is used in the prediction of detonation pressure (P_d) [7]. For example, ΔH_e is calculated:

$$\Delta H_e = \sum \Delta H_{f(\text{product})} - \sum \Delta H_{f(\text{explosive})} \quad (1)$$

The prediction of thermochemical properties to within “chemical accuracy” (usually defined as theoretical values with mean absolute deviation (MAD) within 1.0 kcal mol⁻¹ from experimen-

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tal data for main group species) using computational chemistry ensures that experimental efforts are focused on promising compounds exhibiting required enhanced performance. Since the development, manufacture, testing and fielding of a new energetic material is costly in terms of time and money, using accurate energetics to eliminate poor candidates lacking required sensitivity or having performance problems through theoretical predictions at the early stages of development is highly desirable. Computational chemistry provides an effective means for the prediction of gas phase $\Delta H_{f(g)}^\circ$ for energetic species. Any chosen methods, however, must first demonstrate utility, reliability, and accuracy for the prediction of energetic properties before being utilized in the prediction of the energetic behavior of species not yet fully characterized experimentally.

In a study by Byrd and Rice [8], the $\Delta H_{f(g)}^\circ$ of energetic materials including nitroaliphatics, nitroaromatics, nitroamines, nitrotriazoles, nitrofurans, nitrate esters, nitrites, azidoaliphatics, azidoaromatic, and C-nitroso species were predicted. An objective of the study was to determine the impact of methodological choice on the $\Delta H_{f(g)}^\circ$, with the goal of identifying a suitable strategy of studying CHNO systems. The methodology used by the authors comprised a semi-empirical approach to obtaining $\Delta H_{f(g)}^\circ$ from quantum mechanical energies using a training set for the parameterization of the method. However, cautions must be exercised in utilizing this method on compounds that are not contained in the training set due to this parameterization. B3LYP/6-31G* was used for geometry optimization in the method while an increase in basis set size from 6-31G* to 6-311++G(2df,p) was used for single point energy calculations to give slightly improved $\Delta H_{f(g)}^\circ$. The root mean squared (RMS) deviation improved from 3.1 to 2.9 kcal mol⁻¹ (using a so-called group-equivalent method) with respect to experimental $\Delta H_{f(g)}^\circ$. The dependence of the training set on the methods was also investigated with the conclusion that molecules not included in the training set (compounds containing tetrazole rings, doubly bonded NH groups, and nitrogen linked bridges) tend to result in an increased RMS deviation by as much as one order of magnitude when compared with experimental $\Delta H_{f(g)}^\circ$. The authors' semi-empirical atom- and group-equivalent methods are only viable for CHNO molecules which display properties related to those in the training set, eliminating large classes of energetic compounds such as highly nitrogen-rich compounds.

Identifying computationally feasible methodology to quantitatively predict $\Delta H_{f(g)}^\circ$ has continued to be of much interest. The Byrd and Rice study [8] shows that increasing basis set size and introducing a group equivalence approach, which concomitantly includes reliance on empirically optimized parameters, could lead to a decrease in MAD from experimental values. However, to consistently obtain chemical accuracy for $\Delta H_{f(g)}^\circ$, a high level electron correlation method such as coupled cluster with singles, doubles and quasi-perturbative triples excitations [CCSD(T)] should be used in conjunction with a very large basis set [9]. Alternatively, a series of single point CCSD(T) energies can be computed and extrapolated to the asymptotic complete basis set (CBS) limit, the point at which errors arising from basis set incompleteness have been removed leaving only the intrinsic error in the method utilized. But using CCSD(T) with a large basis set quickly becomes too costly as molecule size increases, and an alternative strategy is to use *ab initio* composite methods.

Composite methods use less sophisticated theories in conjunction with a series of basis sets to approximate results that would be obtained with higher levels of theory but at significantly reduced computational costs (i.e., reduced CPU time, memory, and disk space requirements). A few representative *ab initio* composite methods include the Weizmann-*n* (*Wn*), High-accuracy extrapolated *ab initio* thermochemistry (HEAT), and the Gaussian-*n* (*Gn*) methods. The *Wn* method of Martin and co-workers [10–13] and

the HEAT method of Stanton and co-workers [14,15] use a series of coupled cluster calculations with an objective of achieving accuracy comparable to full configuration interaction (FCI)/CBS limit (within 0.1 kJ mol⁻¹ of reliable experimental values). The drawback of the *Wn* and HEAT methods is their exorbitant computational costs, rendering these methods impractical or unfeasible for molecules with more than a couple of non-hydrogen atoms. The *Gn* methods of Pople and co-workers [16–22] are based on the less expensive Møller–Plesset perturbation theory (second or fourth order) reference energy. The *Gn* methods have been shown to be accurate within 1–2 kcal mol⁻¹ of experimental values for energetic properties, such as enthalpies of formation, ionization potentials, electron and proton affinities. The *Gn* methodologies however make use of empirical high-level corrections (HLCs). For most *Gn* approaches, the HLC is a parameter fit to decrease the MAD for a set of energetic properties (G2/97 test set for the G2, G3 methods and a subset of G5/03 for the G4 method) from corresponding experimental values. Subsequently, the HLC has been shown to account mostly for basis set incompleteness error in the composite method [23]. A possible consequence of fitting HLC to experimental values for a specific set of molecules is uncertain performance when the *Gn* methods are applied to novel molecules that appreciably differ from the test set. There is thus a need for composite methodology based only on first principle solution of the Schrödinger equation.

Our group has developed an *ab initio* composite method free from empirical parameters called the correlation consistent Composite Approach (ccCA) [23–26]. The method has been successful in the prediction of energetic properties, even where other composite approaches have had difficulties (e.g., s-block [27]) or may be undeveloped or in their infancy (e.g., for transition metal species [25,28]). The ccCA utilizes the correlation consistent basis sets [29,30] which are extrapolated to the CBS limit and MP2 calculations to obtain a reference energy upon which the composite method is based. An example of the success of the ccCA methodology is for the G3/99 test set [24], which included 222 enthalpies of formation, where ccCA resulted in a MAD of 0.96 kcal mol⁻¹ (ccCA-P) and 0.97 kcal mol⁻¹ (ccCA-S4), an improvement in comparison to the G3 method with a MAD of 1.16 kcal mol⁻¹.

Recently Kiselev and Gritsan [31] computed $\Delta H_{f(g)}^\circ$ for nitroalkanes, their isomers and radical forms using the G2 [18], G3 [19,32], and G2M(CC5) [33] composite methods. B3LYP/6-31+G(d,p), B3LYP/6-311G(d,p), MPW1B95/6-31+G(d,p) [34], and MPWB1K/6-31+G(d,p) [34] density functional theory methods were also utilized. Though their molecule set included fourteen neutral and four radical compounds that contain one or more NO₂ or ONO groups, experimental values are only available for eight of these species. More recent experimental $\Delta H_{f(g)}^\circ$ for two of these molecules, dinitromethane (−9.2 ± 0.3 kcal mol⁻¹) and trinitromethane (5.7 ± 0.3 kcal mol⁻¹), have been determined by Miroshnichenko et al. [35]. Of the eight molecules with available experimental values (including the updated experimental values for dinitromethane and trinitromethane), the G3 method resulted in a MAD of 1.0 kcal mol⁻¹, which is within the desired threshold of 1.0 kcal mol⁻¹. The B3LYP/6-311G(d,p) method, on the other hand, resulted in a MAD of 5.7 kcal mol⁻¹ while MPWB1K/6-31+G(d,p) method lead to an outrageously high MAD of 27.0 kcal mol⁻¹ for the same species.

In this study, 40 R-NO_x and 5 heterocyclic tetrazine-containing species were examined using the ccCA, G3(MP2) and G3 methods. The R-NO_x compounds contain 3–15 non-hydrogen atoms and include several well-known explosive compounds like RDX, 1-methyl-4-nitrobenzene (PNT), and *N*-methyl-*N*-nitromethanamine (DMNO). 25 of the R-NO_x species in the Byrd and Rice study [8] are in this set of 40 species. As well, the $\Delta H_{f(g)}^\circ$ for 5 heterocyclic tetrazine-containing species, for which there are limited experimental studies, have been predicted.

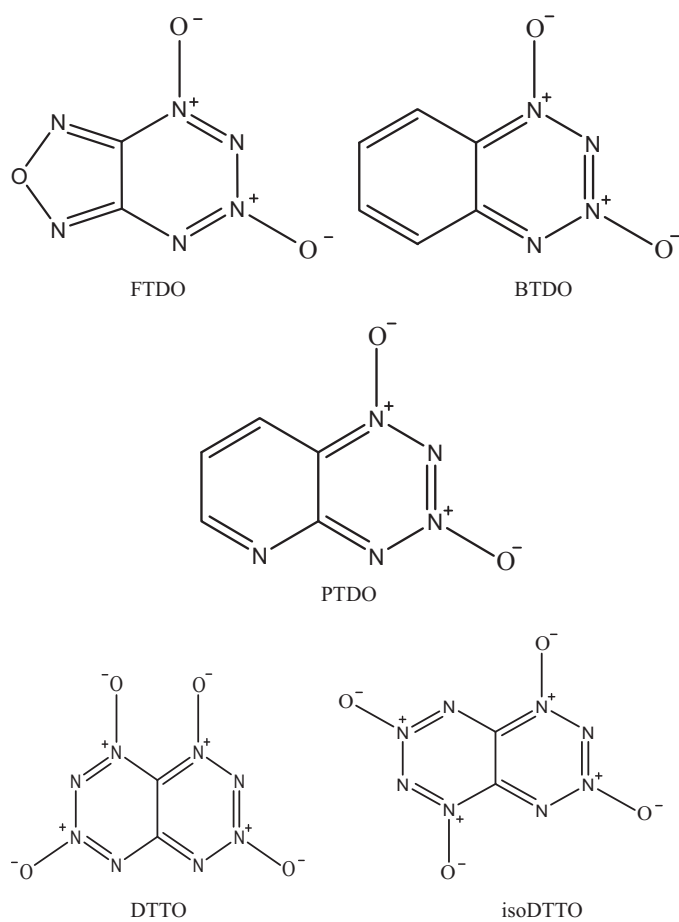


Fig. 1. Heterocyclic tetrazine-containing compounds.

Tetrazine compounds are of high nitrogen content and produce nitrogen gas as the main combustion product rather than carbon monoxide and other toxic gases and are thus more “environmentally friendly” explosives. In addition to their military and commercial uses, they are also used in the pyrotechnics of smokeless and more vibrant fireworks due to their almost carbon-free combustion [36]. Tetrazine explosives are known to be highly endothermic (for instance, $\Delta H_{f(g)}^\circ = +211.0 \text{ kcal mol}^{-1}$ for 3,6-bis(1H-1,2,3,4-tetrazole-5-ylamino)-s-tetrazine) and usually exhibit high insensitivity towards increased temperature, impact, and friction [4,37,38]. An example is furazano-1,2,3,4-tetrazine-1,3-dioxide (FTDO) that has been considered [39] as a promising high energy additive candidate for increasing the momentum of propellants and as a component of energetic plasticizers. Teselkin [39] has studied the sensitivity of FTDO and has compared its critical initial pressure with those of well-known secondary high explosives like cyclotetramethylene-tetranitramine (also known as HMX) and pentaerythritol tetranitrate (PETN). The study revealed that FTDO has a relatively high sensitivity, similar to that of lead azide, a known sensitive compound used in detonators to initiate secondary explosives. Thus, this suggests that studies may discover better insensitive tetrazine compounds. There have been a number of studies [40–43] on the synthesis and characterization of novel tetrazine compounds. However, additional insight would be gained by a computational study of these species. Thus, in this study, the $\Delta H_{f(g)}^\circ$ are predicted for several tetrazine compounds (Fig. 1) [4,38,39,43–47]: ditetrazinetetroxide (DTTO), iso-ditetrazinetetroxide (isoDTTO), FTDO, pyrido[2,3-e]-1,2,3,4-tetrazine-1,3-dioxide (PTDO), and

benzotetrazine-1,3-dioxide (BTDO) that may have potential use as highly energetic species.

2. Computational methods

Geometry optimizations and frequency calculations were performed for all of the molecules using B3LYP in combination with the cc-pVTZ basis sets. The zero-point vibrational energies and enthalpy corrections were scaled by a factor of 0.9890 [26], to account for deficiencies in the harmonic approximation. Single-point calculations were carried out at the B3LYP/cc-pVTZ optimized geometries for each of the ccCA steps [26], which include a series of MP2/aug-cc-pVnZ (where $n = D, T, Q$) calculations for which the SCF and MP2 energies were then extrapolated to the CBS limit. A two point exponential extrapolation scheme developed by Feller and co-workers [48,49] was used for the SCF extrapolation:

$$E(n) = E_{\text{HF-CBS}} + B \exp(-1.63n) \quad (2)$$

Two extrapolation schemes that resulted in the lowest MAD for the G3/99 test set [24] in an earlier study were considered for the extrapolation of the MP2 energies. The first was a mixed exponential/Gaussian formula (ccCA-P) [50], also known as the Peterson extrapolation:

$$E(n) = E_{\text{CBS}} + B \exp[-(n-1)] + C \exp[-(n-1)^2] \quad (3)$$

The second was an extrapolation based on the cubic inverse power of the highest angular momentum in the basis set (ccCA-S3) [12,51]

$$E(l_{\text{max}}) = E_{\text{CBS}} + \frac{B}{(l_{\text{max}})^3} \quad (4)$$

A mixed scheme was also used which was the arithmetic mean of the Schwartz-3 (ccCA-S3) and Peterson (ccCA-P) schemes, hereafter referred to as the ccCA-PS3 scheme, and has been shown in recent studies to be successful at reproducing experimental results [26]. The ccCA-PS3 scheme has proven useful as the Peterson extrapolation tends to overestimate while the Schwartz-3 extrapolation tends to underestimate the CBS limit [26]. In the ccCA-P formula (Eq. (3)), $n = D, T, Q$, corresponding to the ζ -level of the aug-cc-pVnZ basis set (for the extrapolation of the reference SCF, $n = T, Q$) and in the ccCA-S3 formula (Eq. (4)) the l_{max} variable represents the highest angular momentum in the basis set functions.

The Gaussian 03 program package [52] has been used for all calculations. To provide comparison to ccCA results, G3 [32] and G3(MP2) [20] calculations have been performed. The $\Delta H_{f(g)}^\circ$ have been calculated using an atomization energy approach. The atomic enthalpies of formation $\Delta H_f^\circ(0\text{K})$ of elemental carbon, hydrogen, oxygen and nitrogen utilized are 170.11 [53], 51.63, 58.99 and 112.53 kcal mol^{-1} [54], respectively. The mean absolute deviations have been used as an assessment of chemical accuracy for the methods in this study.

3. Results and discussion

The $\Delta H_{f(g)}^\circ$ of the molecules in our test set have been reported in three tables: R-NO₂ (Table 1), R-ONO (Table 2), and R-ONO₂ (Table 3). Table 4 includes the MADs for all molecules in this study, including these three families of molecules. The MAD for each of the extrapolation schemes using the ccCA method is also shown in Table 4. The ccCA-PS3 variant has proven to be the most effective for the highly energetic nitrogen-containing species; hence, the MAD reported for the ccCA method in the remainder of this paper will be the PS3 scheme.

The overall MAD for the nitro-molecules (Table 1) is 1.2 kcal mol^{-1} using the ccCA method, 1.8 kcal mol^{-1} for the G3(MP2) approach, and 1.3 kcal mol^{-1} with the G3 method when

Table 1
The enthalpies of formation (kcal mol⁻¹) of nitro compounds calculated by G3, G3(MP2) and variants of ccCA method.

Molecule	ccCA-P	ccCA-S3	ccCA-PS3	G3	G3(MP2)	Expt. ^a
Nitrogen dioxide	9.3	8.5	8.9	8.1	9.1	8.1 ± 0.2 ^b
Nitroamine	0.8	-0.6	0.1	1.9	3.8	-0.7 ^c
DMNO	-0.8	-3.1	-1.9	-1.4	1.1	-1.2 ± 0.3 ^d
Nitromethane	-17.4	-18.8	-18.1	-17.7	-16.0	-17.8 ± 0.2 ^e
Dinitromethane	-9.2	-11.4	-10.3	-11.2	-8.1	-9.2 ± 0.3 ^e
Trinitromethane	4.2	1.2	2.7	0.6	5.4	5.7 ± 0.3 ^e
Tetranitromethane	25.6	22.0	23.8	18.8	25.6	19.7 ± 0.4 ^e
Nitroethane	-24.5	-26.3	-25.4	-25.5	-23.8	-24.4 ± 1.0 ^f
<i>n</i> -Nitropropane	-29.6	-31.9	-30.8	-30.6	-28.8	-29.6 ± 0.2 ^g
Isonitropropane	-32.7	-35.0	-33.9	-33.8	-31.9	-33.2 ± 0.2 ^g
1,3-Dinitropropane	-30.9	-34.0	-32.5	-32.5	-29.3	-32.4 ± 0.4 ^m
2,2-Dinitropropane	-31.4	-34.4	-32.9	-34.7	-31.0	-32.1 ± 0.5 ^m
<i>n</i> -Nitrobutane	-34.1	-36.9	-35.5	-35.0	-33.2	-34.4 ± 0.4 ^g
1,4-Dinitrobutane	-36.2	-39.8	-38.0	-39.1	-35.9	-38.9 ± 0.7 ^m
<i>n</i> -Nitropentane	-38.8	-42.0	-40.4	-40.3	-38.5	-39.4 ± 0.5 ^m
Nitrocyclohexane	-36.1	-39.6	-37.8	-38.2	-36.4	-38.1 ± 0.2 ^h
<i>n</i> -Nitropiperidine	-7.4	-10.9	-9.1	-9.1	-6.7	-10.6 ± 0.6 ⁱ
RDX	47.8	42.8	45.3	42.7	49.8	45.8 ^j
Nitrobenzene	17.7	14.6	16.2	15.2	15.2	16.1 ± 0.1 ⁱ
<i>m</i> -Dinitrobenzene	16.4	12.5	14.5	12.3	14.1	12.9 ± 0.4 ^k
<i>p</i> -Dinitrobenzene	16.3	12.5	14.4	12.5	14.3	13.3 ± 0.2 ^h
<i>o</i> -nitroaniline	16.5	13.0	14.8	14.7	15.5	15.0 ± 1.0 ^l
<i>m</i> -Nitrotoluene	10.1	6.5	8.3	6.9	7.1	4.1 ^c
<i>p</i> -Nitrotoluene (PNT)	9.8	6.3	8.0	6.7	7.0	7.4 ± 1.0 ⁿ
2,6-Dinitrotoluene	13.6	9.3	11.5	7.9	10.3	9.6 ^c
<i>o</i> -nitrophenol	-27.8	-31.2	-29.5	-30.4	-29.5	-31.6 ± 0.3 ⁱ
<i>m</i> -Nitrophenol	-24.3	-27.6	-25.9	-27.0	-26.4	-25.2 ± 0.4 ⁱ
2,4-Dinitrophenol	-29.9	-34.0	-32.0	-34.1	-31.4	-30.6 ± 1.2

^a NIST Chemistry WebBook, NIST Standard Reference Database Number 69; Linstrom, P.J., Mallard, W.G., Eds.; National Institute of Standards and Technology, Gaithersburg, MD, June 2009; 20899 (<http://webbook.nist.gov/chemistry/>).

^b Ref. [55].

^c Ref. [56].

^d Ref. [57].

^e Ref. [35].

^f Ref. [58].

^g Ref. [59].

^h Ref. [61].

ⁱ Ref. [62].

^j Ref. [63].

^k Ref. [64].

^l Ref. [65].

^m Ref. [60].

ⁿ Ref. [66].

Table 2
The enthalpies of formation (kcal mol⁻¹) of nitrite compounds calculated by G3, G3(MP2) and variants of ccCA methods compared with experimental values.

Molecule	ccCA-P	ccCA-S3	ccCA-PS3	G3	G3(MP2)	Expt. ^a
Methylnitrite	-15.7	-17.1	-16.4	-15.5	-14.6	-15.6 ± 0.2
Ethyl nitrite	-23.1	-24.9	-24.0	-23.2	-22.2	-25.9
<i>n</i> -Propylnitrite	-27.8	-30.1	-28.9	-28.1	-27.1	-28.4 ± 1.0
Isopropylnitrite	-31.3	-33.6	-32.5	-32.2	-31.6	-31.9 ± 1.0
<i>n</i> -Butylnitrite	-32.6	-35.3	-34.0	-33.0	-32.0	-34.8 ± 1.0
Isobutylnitrite	-34.5	-37.2	-35.9	-35.2	-34.1	-36.1 ± 1.0
<i>sec</i> -Butylnitrite	-34.4	-37.1	-35.8	-35.5	-34.2	-36.5 ± 1.0
<i>t</i> -Butylnitrite	-39.5	-42.3	-40.9	-41.1	-39.7	-41.0 ± 1.0

^a NIST Chemistry WebBook, NIST Standard Reference Database Number 69; Linstrom, P.J., Mallard, W.G., Eds.; National Institute of Standards and Technology, Gaithersburg, MD, June 2009; 20899 (<http://webbook.nist.gov/chemistry/>).

Table 3
The enthalpies of formation (kcal mol⁻¹) of nitrate compounds calculated by G3, G3(MP2) and variants of ccCA methods compared with experimental values.

Molecules	ccCA-P	ccCA-S3	ccCA-PS3	G3	G3(MP2)	Expt. ^a
Nitric acid	-32.1	-33.3	-32.7	-31.7	-29.8	-32.1 ± 0.1
Methylnitrate	-28.8	-30.5	-29.7	-29.6	-27.3	-29.2 ± 0.3
Ethyl nitrate	-36.7	-38.8	-37.8	-37.8	-35.5	-37.0 ± 0.8
<i>n</i> -Propylnitrate	-41.3	-43.9	-42.6	-42.6	-40.3	-41.6 ± 0.3 ^b

^a NIST Chemistry WebBook, NIST Standard Reference Database Number 69; Linstrom, P.J., Mallard, W.G., Eds.; National Institute of Standards and Technology, Gaithersburg, MD, June 2009; 20899 (<http://webbook.nist.gov/chemistry/>).

^b Pedley, J.B., Naylor, R.D., Kirby, S.P. *Thermochemical data of organic compounds*; Chapman and Hall: London; New York, 1986.

Table 4

The calculated MAD (kcal mol⁻¹) of the enthalpies of formation for all 40 molecules compared to experimental values.

	ccCA-P	ccCA-S3	ccCA-PS3	G3	G3(MP2)
Nitro	1.9	1.7	1.2	1.3	1.8
Nitrite	1.4	1.2	0.7	0.9	1.8
Nitrate	0.3	1.7	0.7	0.7	1.8
Overall	1.6	1.6	1.1	1.2	1.8

compared to the experimental $\Delta H_{f(g)}^\circ$. Since ccCA is MP2-based, its performance is best compared with that of G3(MP2), another MP2 based method, rather than with the MP4 based G3 method. The maximum absolute deviation for G3(MP2) is 5.9 kcal mol⁻¹, corresponding to tetranitromethane, while ccCA achieves a MAD of 4.1 kcal mol⁻¹ for this compound. The G3 approach shows a deviation of only 0.9 kcal mol⁻¹ for the same compound, suggesting that a higher level reference correlation method than MP2 is needed for this molecule. Interestingly, the G3 HLC is -38.1 kcal mol⁻¹ while the HLC for G3(MP2) is -46.6 kcal mol⁻¹, indicating the significant reliance (but success of G3 for this molecule) on experimental parameterization. However, for the study of energetic properties of compounds without reliable experimental data, which is a major objective of this study, ccCA provides a useful approach, as it does not rely upon empirical parameters such as a HLC. The ccCA method is shown to be more accurate than G3(MP2), the more comparable method. If tetranitromethane is removed from the set of molecules, ccCA would result in a MAD, for the ensuing subset, of 1.1 kcal mol⁻¹, G3 would remain at 1.3 kcal mol⁻¹, and G3(MP2) would have a MAD of 1.6 kcal mol⁻¹. The ccCA method also results in a deviation of 4.2 kcal mol⁻¹ for *m*-nitrotoluene for which the G3 method is in disagreement by 2.8 kcal mol⁻¹ relative to the experimental value. The apparent consistency of the theoretical methods leads to the suggestion that experimental values could have been underestimated. For RDX, a well known and studied explosive, ccCA is shown to deviate by 0.5 kcal mol⁻¹ from the experimental value. G3 differs from the experiment by 3.1 kcal mol⁻¹ while G3(MP2) has the highest absolute deviation of 4.0 kcal mol⁻¹. Overall, for the R-NO₂ compounds, the ccCA and G3 methods are quantitatively satisfactory for the study of nitro-containing energetic molecules.

Table 2 contains the results for the R-ONO compounds of the test set. The results show that the ccCA method leads to a MAD of 0.7 kcal mol⁻¹ from the experimental values, the G3 method results in a MAD of 0.9 kcal mol⁻¹ while the MAD for G3(MP2) method is 1.8 kcal mol⁻¹. The ccCA method is within the threshold of chemical accuracy for seven of the eight nitrite molecules considered. The maximum absolute deviation is 3.7 kcal mol⁻¹ for G3(MP2) while G3 and ccCA exhibit maximum absolute deviations of 2.7 and 1.9 kcal mol⁻¹, respectively, all corresponding to the molecule ethyl nitrite.

In Table 3, results for the R-ONO₂ molecules are presented. The ccCA method yields a MAD of 0.7 kcal mol⁻¹, G3 leads to a MAD of 0.7 kcal mol⁻¹, while the G3(MP2) method achieves a MAD of 1.8 kcal mol⁻¹. The ccCA and G3 methods show a maximum absolute deviation of 1.0 kcal mol⁻¹ for *n*-propyl nitrate, while G3(MP2) maximum deviation from experimental results is 2.3 kcal mol⁻¹ for nitric acid. Overall, the performances of the ccCA and G3 methods are within the desired chemical accuracy when compared to experiment.

Table 4 contains the summary of the MAD for $\Delta H_{f(g)}^\circ$ for the 40 compounds studied. The G3 approach, which is MP4 based, leads to a MAD of 1.2 kcal mol⁻¹. The ccCA method exhibits a MAD of 1.1 kcal mol⁻¹, indicating that it is a reliable method to predict and validate $\Delta H_{f(g)}^\circ$ for highly energetic nitrogen-containing compounds. The G3(MP2) method results in a MAD of 1.8 kcal mol⁻¹ for the entire test set, which is greater than the MAD obtained

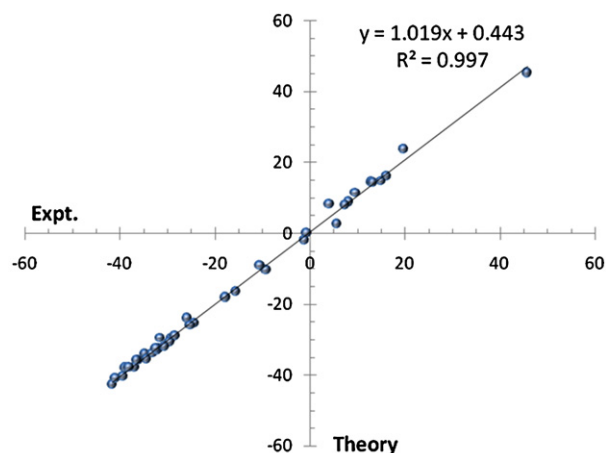


Fig. 2. Theoretical vs. experimental $\Delta H_{f(g)}^\circ$ (kcal mol⁻¹) calculated using ccCA-PS3.

Table 5

The predicted enthalpies (kcal mol⁻¹) of formation of tetrazine-containing compounds using G3 and variants of ccCA methods.

Molecule	ccCA-P	ccCA-S3	ccCA-PS3	G3
FTDO	178.2	174.7	176.5	178.3
PTDO	139.6	135.6	137.6	137.3
BTDO	124.1	120.0	122.0	121.5
DTTO	234.4	230.0	232.2	233.0
isoDTTO	233.3	228.8	231.1	232.1

with the ccCA method even though both are based on MP2 method. The experimental $\Delta H_{f(g)}^\circ$ plotted against the ccCA computed values (Fig. 2) shows a linear regression coefficient (R^2) value of 0.996. The similarities observed in the MAD of the ccCA method compared to the G3 method, coupled with the aforementioned advantages of ccCA over G3, encourage our recommendation of ccCA for the prediction of highly energetic nitrogen-containing compounds.

The ccCA and G3 methods have also been utilized in the determination of the $\Delta H_{f(g)}^\circ$ for five novel tetrazine compounds. The optimal synthetic methods for these compounds are currently under studies [4,38,39,43–47]. The results for the five potential insensitive heterocyclic explosives are shown in Table 5. The enthalpies of formation for FTDO, PTDO, BTDO and isomeric 1,2,3,4,5,6,7,8-octazanaphthalene tetroxides (DTTO and isoDTTO) (Fig. 1) have been computed using the G3 and ccCA methods due to their low MAD as found in this study. The predicted $\Delta H_{f(g)}^\circ$ (298 K) for FTDO using the ccCA approach is 176.5 kcal mol⁻¹, in good agreement with 178.3 kcal mol⁻¹ of the G3 method, but at variance with 171.7 and 168.8 kcal mol⁻¹ of G2 and CBS-QB3 methods, respectively, as reported by Kiselev et al. [44]. The ccCA method predicts the $\Delta H_{f(g)}^\circ$ for PTDO, BTDO, DTTO and isoDTTO as 137.6, 122.0, 232.2, and 231.1 kcal mol⁻¹ while the results obtained using the G3 method for these compounds are 137.3, 121.5, 233.0, and 232.1 kcal mol⁻¹, respectively.

4. Conclusion

Accurate prediction of the enthalpy of formation of potential energetic compounds will assist in the discovery of materials with low sensitivity to reduce disastrous premature explosions. Formulation of high explosives with enhanced performances can be improved by using chemically accurate $\Delta H_{f(g)}^\circ$ in the calculation of explosive properties like VOD, T_e , ΔH_e and P_d . Three composite methods have been utilized in this study, the G3, G3(MP2), and ccCA methods, to determine an effective method able to accurately

predict the gas phase ΔH_f° at 298 K for highly energetic nitrogen-containing compounds.

A test set of 40 nitrogen-containing molecules was divided into three subsets in order to assess the energetic differences between the different types of nitrogen-containing groups (nitro, nitrate, and nitrite) in the study. The gas phase $\Delta H_{f(g)}^\circ$ have also been predicted for five heterocycle-tetrazine compounds which have no experimental energetic data available. Due to their comparable accuracies and low MAD, the ccCA and G3 methods have been used to predict the $\Delta H_{f(g)}^\circ$ for five tetrazine-based heterocyclic compounds with high-nitrogen content and desirable endothermic properties. The ccCA method predicts the $\Delta H_{f(g)}^\circ$ for FTDO, PTDO, BTDO, DTTO and isoDTTO as 176.5, 137.6, 122.0, 232.2 and 231.1 kcal mol⁻¹, respectively, while the G3 method results in 178.3, 137.3, 121.5, 233.0, and 232.1 kcal mol⁻¹, respectively, indicating a very good agreement between the two methods. The ccCA method, the only composite method in this study that does not depend on empirically derived parameterization, has been shown to produce highly accurate $\Delta H_{f(g)}^\circ$ for highly energetic nitrogen-rich compounds. We recommend the use of ccCA in future studies of highly energetic nitrogen-rich species. Additionally, based solely on their very high positive $\Delta H_{f(g)}^\circ$, DTTO and isoDTTO are good candidates for further consideration as insensitive high explosives.

Acknowledgements

The authors gratefully acknowledge the support of the National Science Foundation (CHE-0809762). The authors acknowledge the support of the National Science Foundation Chemistry Research Instrumentation and Facilities, NSF CRIF (CHE-0741936), for computing resources.

References

- [1] Department of Army Technical Manual, Military Explosives, Department of Army (Ed.), Headquarters, Department of the Army, Washington D.C., 1990.
- [2] Military explosives in Department of Army (Ed.), Technical Manual: Military Explosives, Washington, D.C., 1984, pp. 2–13.
- [3] R.D. Agrawal, Organic Chemistry of Explosives, John Wiley & Sons Ltd., Chichester, 2007.
- [4] D.E. Chavez, M.A. Hiskey, D.L. Naud, Tetrazine Explosives, Propell. Explos. Pyrotech. 29 (2004) 209–215.
- [5] V. LoPresti, "Playing" with Fire, Los Alamos Research Quarterly, Summer 2003.
- [6] P.F. Pagoria, G.S. Lee, A.R. Mitchell, R.D. Schmidt, A review of energetic materials synthesis, Thermochim. Acta 384 (2002) 187–204.
- [7] H. Muthurajan, R. Sivabalan, M.B. Talawar, M. Anniyappan, S. Venugopalan, Prediction of heat of formation and related parameters of high energy materials, J. Hazard. Mater. 133 (2006) 30–45.
- [8] E.F. Byrd, B.M. Rice, Improved prediction of heats of formation of energetic materials using quantum mechanical calculations, J. Phys. Chem. A 110 (2006) 1005–1013.
- [9] J.M.L. Martin, P.R. Taylor, Benchmark quality total atomization energies of small polyatomic molecules, J. Chem. Phys. 106 (1997) 8620–8623.
- [10] A.D. Boese, M. Oren, O. Atasoylu, J.M.L. Martin, M. Kallay, J. Gauss, W3 theory: robust computational thermochemistry in the kJ/mol accuracy range, J. Chem. Phys. 120 (2004) 4129–4141.
- [11] A. Karton, E. Rabinovich, J.M.L. Martin, B. Ruscic, W4 theory for computational thermochemistry: in pursuit of confident sub-kJ/mol predictions, J. Chem. Phys. 125 (2006) 144108–144117.
- [12] J.M.L. Martin, G. de Oliveira, Towards standard methods for benchmark quality ab initio thermochemistry – W1 and W2 theory, J. Chem. Phys. 111 (1999) 1843–1856.
- [13] S. Parthiban, J.M.L. Martin, Assessment of W1 and W2 theories for the computation of electron affinities, ionization potentials, heats of formation, and proton affinities, J. Chem. Phys. 114 (2001) 6014–6029.
- [14] Y.J. Bomble, J. Vazquez, M. Kallay, C. Michauk, P.G. Szalay, A.G. Csaszar, J. Gauss, J.F. Stanton, High-accuracy extrapolated ab initio thermochemistry. II. Minor improvements to the protocol and a vital simplification, J. Chem. Phys. 125 (2006) 064108–64118.
- [15] M.E. Harding, J. Vazquez, B. Ruscic, A.K. Wilson, J. Gauss, J.F. Stanton, High-accuracy extrapolated ab initio thermochemistry. III. Additional improvements and overview, J. Chem. Phys. 128 (2008) 15.
- [16] L.A. Curtiss, K. Raghavachari, P.C. Redfern, J.A. Pople, Assessment of Gaussian-2 and density functional theories for the computation of enthalpies of formation, J. Chem. Phys. 106 (1997) 1063–1079.
- [17] L.A. Curtiss, K. Raghavachari, P.C. Redfern, J.A. Pople, Assessment of Gaussian-3 and density functional theories for a larger experimental test set, J. Chem. Phys. 112 (2000) 7374–7383.
- [18] L.A. Curtiss, K. Raghavachari, G.W. Trucks, J.A. Pople, Gaussian-2 theory for molecular energies of first- and second-row compounds, J. Chem. Phys. 94 (1991) 7221.
- [19] L.A. Curtiss, P.C. Redfern, K. Raghavachari, Assessment of Gaussian-3 and density-functional theories on the G3/05 test set of experimental energies, J. Chem. Phys. 123 (2005) 124107.
- [20] L.A. Curtiss, P.C. Redfern, K. Raghavachari, V. Rassolov, J.A. Pople, Gaussian-3 theory using reduced Möller–Plesset order, J. Chem. Phys. 110 (1999) 4703–4709.
- [21] J.A. Pople, M. Head-Gordon, D.J. Fox, K. Raghavachari, L.A. Curtiss, Gaussian-1 theory: a general procedure for prediction of molecular energies, J. Chem. Phys. 90 (1989) 5622–5629.
- [22] K. Raghavachari, L.A. Curtiss, E.D. Clifford, F. Gernot, S.K. Kwang, E.S. Gustavo, Theory and Applications of Computational Chemistry, Elsevier, Amsterdam, 2005, pp. 785–812.
- [23] N.J. DeYonker, T.R. Cundari, A.K. Wilson, The correlation consistent composite approach (ccCA): an alternative to the Gaussian-*n* methods, J. Chem. Phys. 124 (2006) 114104.
- [24] N.J. DeYonker, T. Grimes, S. Yockel, A. Dinescu, B. Mintz, T.R. Cundari, A.K. Wilson, The correlation-consistent composite approach: application to the G3/99 test set, J. Chem. Phys. 125 (2006) 104111.
- [25] N.J. DeYonker, T.G. Williams, A.E. Imel, T.R. Cundari, A.K. Wilson, Accurate thermochemistry for transition metal complexes from first-principles calculations, J. Chem. Phys. 131 (2009) 024106–24109.
- [26] N.J. DeYonker, B.R. Wilson, A.W. Pierpont, T.R. Cundari, A.K. Wilson, Towards the intrinsic error of the correlation consistent Composite Approach (ccCA), Mol. Phys. 107 (2009) 1107–1121.
- [27] N.J. DeYonker, D.S. Ho, A.K. Wilson, T.R. Cundari, Computational s-block thermochemistry with the correlation consistent composite approach, J. Phys. Chem. A 111 (2007) 10776–10780.
- [28] N.J. DeYonker, K.A. Peterson, G. Steyl, A.K. Wilson, T.R. Cundari, Quantitative computational thermochemistry of transition metal species, J. Phys. Chem. A 111 (2007) 11269–11277.
- [29] A.K. Wilson, T. van Mourik, T.H. Dunning Jr., Gaussian basis sets for use in correlated molecular calculations. VI. Sextuple zeta correlation consistent basis sets for boron through neon, J. Mol. Struct. (THEOCHEM) 388 (1996) 339–349.
- [30] K.A. Peterson, T.H. Dunning Jr., Accurate correlation consistent basis sets for molecular core-valence correlation effects: the second row atoms Al–Ar, and the first row atoms B–Ne revisited, J. Chem. Phys. 117 (2002) 10548–10560.
- [31] V.G. Kiselev, N.P. Gritsan, Theoretical study of the nitroalkane thermolysis. 1. Computation of the formation enthalpy of the nitroalkanes, their isomers and radical products, J. Phys. Chem. A 112 (2008) 4458–4464.
- [32] L.A. Curtiss, P.C. Redfern, K. Raghavachari, J.A. Pople, Gaussian-3 theory: a variation based on third-order perturbation theory and an assessment of the contribution of core-related correlation, Chem. Phys. Lett. 313 (1999) 600–607.
- [33] A.M. Mebel, K. Morokuma, M.C. Lin, Modification of the GAUSSIAN-2 theoretical model: the use of coupled-cluster energies, density-functional geometries, and frequencies, J. Chem. Phys. 103 (1995) 7414.
- [34] Y. Zhao, D.G. Truhlar, Hybrid meta density functional theory methods for thermochemistry, thermochemical kinetics, and noncovalent interactions: the MPW1B95 and MPWB1K models and comparative assessments for hydrogen bonding and van der Waals interactions, J. Phys. Chem. A 108 (2004) 6908–6918.
- [35] E.A. Miroshnichenko, T.S. Kon'kova, Y.O. Inozemtsev, V.P. Vorob'eva, Y.N. Matyushin, S.A. Shevelev, Bond energies and formation enthalpies of mono- and polyradicals in nitroalkanes 1. Nitromethanes, Russian Chem. Bull. 58 (2009) 772–776.
- [36] W.M. Koppes, M.E. Sitzmann, Triazolyl-tetrazinyl-aminotriazine compounds useful in pyrotechnic compositions and process thereof, US Patent 6602366 (2003), p. 9.
- [37] K.Y. Lee, C.B. Storm, M.A. Hiskey, M.D. Coburn, An improved synthesis of 5-amino-3-nitro-1H-1,2,4-triazole (ANTA), a useful intermediate for the preparation of insensitive high explosives, J. Energ. Mater. 9 (1991) 415–428.
- [38] D.E. Chavez, M.A. Hiskey, M.H. Huynh, D.L. Naud, S.F. Son, B.C. Tappan, The combustion properties of novel high-nitrogen energetic materials, J. Pyrotech. 23 (2006) 70–80.
- [39] V. Teselkin, Mechanical sensitivity of furazano-1,2,3,4-tetrazine-1,3-dioxide, Combust. Explosion Shock Waves 45 (2009) 632–633.
- [40] A. Pierre, M. Fabien, C. Gilles, V. Marie-Claude, B. Sophie, M.-R. Rachel, Synthesis and properties of new tetrazines substituted by heteroatoms: towards the World's smallest organic fluorophores, Chem. Eur. J. 11 (2005) 5667–5673.
- [41] J. Soloducho, J. Doskocz, J. Cabaj, S. Roszak, Practical synthesis of bis-substituted tetrazines with two pendant 2-pyrrolyl or 2-thienyl groups, precursors of new conjugated polymers, Tetrahedron 59 (2003) 4761.
- [42] N. Saracoglu, Recent advances and applications in 1,2,4,5-tetrazine chemistry, Tetrahedron 63 (2007) 4199–4236.
- [43] A.M. Churakov, V.A. Tartakovsky, Progress in 1,2,3,4-tetrazine chemistry, Chem. Rev. 104 (2004) 2601–2616.
- [44] V. Kiselev, N. Gritsan, V. Zarko, P. Kalmykov, V. Shandakov, Multilevel quantum chemical calculation of the enthalpy of formation of [1,2,5]oxadiazolo[3,4-e][1,2,3,4]-tetrazine-4,6-di-N-dioxide, Combust. Explosion Shock Waves 43 (2007) 562–566.

- [45] K.O.H. Christie, R. Haiges, R.I. Wagner, C.J. Jones, Synthesis of New High-Oxygen Carriers and Ditetrazinetetroxide (DTTO), California University, Los Angeles Department of Chemistry and Biochemistry, 2009.
- [46] V.A. Tartakovsky, I.E. Filatov, A.M. Churakov, S.L. Ioffe, Y.A. Strelenko, V.S. Kuz'min, G.L. Rusinov, K.I. Pashkevich, Synthesis and structures of pyridoannulated 1,2,3,4-tetrazine 1,3-dioxides, Russian Chem. Bull. 53 (2004) 2577–2583.
- [47] O.Y. Smirnov, A.M. Churakov, Y.A. Strelenko, S.L. Ioffe, V.A. Tartakovsky, Nitration and bromination of benzo-1,2,3,4-tetrazine 1,3-dioxides, Russian Chem. Bull. 51 (2002) 1841–1848.
- [48] D. Feller, Application of systematic sequences of wave functions to the water dimer, J. Chem. Phys. 96 (1992) 6104–6114.
- [49] A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, J. Olsen, Basis-set convergence of the energy in molecular Hartree–Fock calculations, Chem. Phys. Lett. 302 (1999) 437–446.
- [50] K.A. Peterson, D.E. Woon, T.H. Dunning Jr., Benchmark calculations with correlated molecular wave functions. IV. The classical barrier height of the $H + H_2 \rightarrow H_2 + H$ reaction, J. Chem. Phys. 100 (1994) 7410–7415.
- [51] T. Helgaker, W. Klopper, H. Koch, J. Noga, Basis-set convergence of correlated calculations on water, J. Chem. Phys. 106 (1997) 9639–9646.
- [52] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, revision C.02, 2004.
- [53] G. Tasi, R. Izsák, G. Matisz, A.G. Császár, M. Kállay, B. Ruscic, J.F. Stanton, The origin of systematic error in the standard enthalpies of formation of hydrocarbons computed via atomization schemes, Chem. Phys. Chem. 7 (2006) 1664–1667.
- [54] L.A. Curtiss, K. Raghavachari, P.W. Deutsch, J.A. Pople, Theoretical study of Si_2H_n ($n = 0–6$) and $Si_2H_n^+$ ($n = 0–7$): appearance potentials, ionization potentials, and enthalpies of formation, J. Chem. Phys. 95 (1991) 2433–2444.
- [55] B. Ruscic, R.E. Pinzon, M.L. Morton, N.K. Srinivasan, M.-C. Su, J.W. Sutherland, J.V. Michael, Active thermochemical tables: accurate enthalpy of formation of hydroperoxyl radical, HO_2 , J. Phys. Chem. A 110 (2006) 6592–6601.
- [56] L.P. Davis, D. Storch, R.M. Guidry, MINDO/3, MNDO and AM1 calculations for nitro compounds, J. Energ. Mater. 5 (1987) 89–142.
- [57] Y.N. Matyushin, I.B. V'Yunova, V.I. Pepekin, A.Y. Apin, Enthalpy of formation of a piperidyl radical, Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya 11 (1971) 2443–2447.
- [58] J.D. Cox, G. Pilcher, Thermochemistry of Organic and Organometallic Compounds, Academic Press, London, 1970.
- [59] D.E. Holcomb, C.L. Dorsey, Thermodynamic properties of nitroparaffins, J. Ind. Eng. Chem. 41 (1949) 2788–2792.
- [60] E.A. Miroshnichenko, V.P. Vorob'eva, Thermochemical Characteristics of Nitroalkanes, Russ. J. Phys. Chem. (Engl. Transl.) 73 (1999) 349–355.
- [61] S.P. Verevkin, Thermochemistry of nitro compounds. Experimental standard enthalpies of formation and improved group-additivity values, Thermochim. Acta 307 (1997) 17–25.
- [62] J.B. Pedley, R.D. Naylor, S.P. Kirby, Thermochemical Data of Organic Compounds, 2nd edition, Chapman and Hall, London, New York, 1986.
- [63] V.I. Pepekin, Y.N. Matyushin, Y.A. Lebedev, Thermochemistry of N-nitro- and N-nitrosoamines of the alicyclic series, Russian Chem. Bull. 23 (1974) 1707–1710.
- [64] I. Nitta, S. Seki, M. Momotani, K. Sato, Vapor pressures of molecular crystals VIII. Aromatic nitro compounds, J. Chem. Soc. Jpn. 71 (1950) 378–382.
- [65] S.G. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, R.D. Levin, W.G. Mallard, J. Phys. Chem. Ref. Data 17 (1988) 1.
- [66] C. Lenchitz, R.W. Velicky, G. Silvestro, L.P. Schlosberg, Thermodynamic properties of several nitrotoluenes, J. Chem. Thermodyn. 3 (1971) 689–692.