A DFT theoretical study of heats of formation and detonation properties of nitrogen-rich explosives

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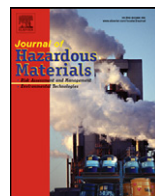**15** PUBLICATIONS   **284** CITATIONS

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A DFT theoretical study of heats of formation and detonation properties of nitrogen-rich explosives

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ABSTRACT

We present density-functional theory predictions and analysis of some properties of synthesized high-nitrogen compounds 3,6-diazido-1,2,4,5-tetrazine (DiAT) and N-oxides of 3,3′-azo-bis(6-amino-1,2,4,5-tetrazine) (DAATO) together with 3,6-di(hydrazino)-1,2,4,5-tetrazine (DHT) and 3,3′-azo-bis(6-amino-1,2,4,5-tetrazine) (DAAT) for which experimental data are available. In this work the reference molecules DHT and DAAT have been studied in order to validate the theoretical approach and facilitate further progress developments for the molecules of interest such as DiAT and DAATO. Geometries of all compounds have been optimized employing the B3LYP density-functional method in conjunction with 6-311++G(3d,3p) basis sets. The energy content of the molecules in the gas phase is evaluated by calculating standard enthalpies of formation, using isodesmic reaction paths. We also include estimates of the condensed-phase heats of formation and heats of sublimation in the framework of the Politzer approach. The obtained results show that DiAT compound has the highest heat of formation (231 kcal/mol) in comparison with those of DHT, DAAT and DAATO molecules. The detonation velocity and pressure have also been estimated for these molecules using the Stine method.

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1. Introduction

In both modern civil and military applications there is a clear need for energetic materials that have superior performance and lower vulnerability to undesired stimuli, i.e. higher insensitivity to thermal shock, friction, and electric discharge. These properties are essential to improve the personnel safety and to reduce the warhead vulnerability problems. A key challenge along that direction is the tendency for performance and insensitivity characteristics to be mutually exclusive [1], with improved insensitivity bringing inferior performance and vice versa, especially within the area of traditional energetic compounds. One promising approach to overcoming that challenge is to explore new energetic compounds with increased nitrogen content, which is the direction pursued by many recent research and development efforts, as reviewed in Refs. [1–4]. The characteristic feature of such high-nitrogen compounds is that, in contrast to traditional energetic molecules, their energy content comes primarily from the high heats of formation due to the large number of energetic N–N and C–N, rather than from the overall heat of combustion (oxidation of carbon backbone). The high-nitrogen compounds also tend to have an additional benefit of being less toxic for the user and the environment, as higher portion of their decomposition products is dinitrogen. An important class of high-nitrogen molecules is heterocyclic compounds [2,3], which have received much recent attention in an energetic materials role due to a very advantageous combination of thermal stability, heat of formation and density, as well as oxygen balance. High-nitrogen compounds are well known by their high positive heats of formation [5–7] as well as their thermal stability [8]. These properties reveal a high performance of these energetic materials. As a bonus, they are less harmful to the environment and users since their combustion reactions will hopefully release non-toxic gas such as N_2.

High-nitrogen compounds investigated in this work are N-oxides of 3,3′-azo-bis(6-amino-1,2,4,5-tetrazine) (DAATO) [9] and 3,6-diazido-1,2,4,5-tetrazine (DiAT) [10], which have been synthesized. However, to the best of our knowledge no experimental data are available for their heats of formation at the solid phase as well as their detonation properties.

In this paper, we present predicted heats of formation for the above compounds in condensed phase and their detonation properties using quantum chemistry calculations, such as the hybrid density-functional theory (DFT) [11]. Reference molecules 3,6-di(hydrazino)-1,2,4,5-tetrazine (DHT) and 3,3′-azo-bis(6-amino-1,2,4,5-tetrazine) (DAAT) for which experimental data are available [12,13] were also studied for purpose of validation of theoretical approaches used for DAATO and DiAT molecules.

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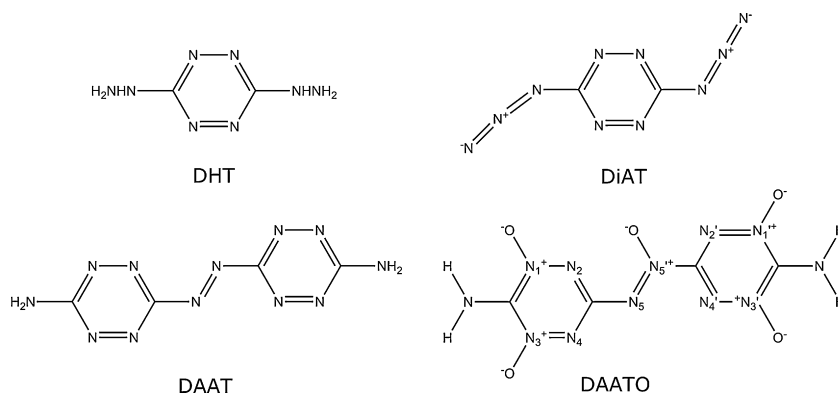 *E-mail address:* Hakima.Abou-Rachid@drdc-rddc.gc.ca (H. Abou-Rachid).

Fig. 1. Chemical structure of molecules in the studied system, where a, b, c, d and e are 0 or 1 and $a + b + c + d + e$ is from 0 to 5.

2. Computational methods and details

All calculations on structural properties of DHT, DiAT, DAAT and DAATO compounds, in Fig. 1, were carried out in the framework of density-functional theory (DFT). In the present work, we have used B3LYP [14–16] hybrid functional, conjunct with 6-311++G(3d,3p) basis sets [17]. The B3LYP density functional has been shown to produce experimental proprieties and is commonly thought to be one of the most reliable of the available density functionals [18–20]. The geometry of molecules were optimized using gradient techniques at the HF/STO-3G, HF/6-31G, B3LYP/6-311G, and B3LYP/6-311++G(3d,3p) levels without symmetry constraints. All calculations were performed using the Gaussian 03 [21] packages.

Harmonic vibrational frequencies were calculated at the same theory level as that are used to fully optimize molecular structures, which enable us to confirm the real minima. A hybrid representation (numerical and analytical) Gaussian basis DFT implementation was used for calculations on electronic density and electrostatic potential in numerical grids with optimized geometric structures of molecules. In this paper, condensed-phase heats of formation $\Delta_f H^\circ_{\text{Solid}}$ were determined using the gas-phase heat of formation and heat of sublimation according to Hess' law of constant heat summation [22]:

$$\Delta_f H^\circ_{\text{Solid}} = \Delta_f H^\circ_{\text{Gas}} - \Delta H_{\text{Sub}} \tag{1}$$

$\Delta_f H^\circ_{\text{Gas}}$ is estimated using isodesmic reactions [23]. An isodesmic reaction is defined as a chemical reaction in which the numbers of electron pairs and the chemical bond types are conserved in the reaction.

The heat of sublimation, $\Delta_f H^\circ_{\text{Sub}}$, is predicted using Politzer approach [24]. Politzer and Murray [25,26] demonstrated that correlations may be established between statistically based quantities of electrostatic potentials (ESP) mapped onto isodensity surfaces of isolated molecules and their heats of sublimation. Rice et al. [27] as well as Byrd and Rice [28] have applied Politzer et al. approach to calculate heats of sublimation of some energetic materials. Politzer et al. assume that heats of sublimation may be estimated by the following empirical expression [29]:

$$\Delta H_{\text{Sub}} = \beta_1 A^2 + \beta_2 \sqrt{\nu \sigma^2_{\text{tot}}} + \beta_3 \tag{2}$$

where A is the molecular surface area, in this approach A is defined to be the isosurface corresponding to the value 0.001 electrons/bohr^3 of electronic density. ν describes the degree of balance between positive and negative potential on the molecular surface, σ^2_{tot} is a measure of variability of the electrostatic potential on the molecular surface. The β_{1-3} parameters are determined from least-squares fitting to reliable values of enthalpies of phase change which is the heat of sublimation. In fact, physical properties such as detonation velocity (D, m/s) and detonation

pressure (P, GPa) were estimated for all molecules of interest in work.

3. Results and discussion

3.1. Gas-phase heats of formation

The gas-phase heats of formation $\Delta_f H^\circ_{\text{Gas}}$ have been evaluated using isodesmic reactions listed below (Table 1). Firstly, since $\Delta_f H^\circ_{\text{Gas}}$ for 1,3,5-triazine, pyridazine, and 1,3-diazine are known it is possible to calculate $\Delta_f H^\circ_{\text{Gas}}$ for 1,2,4-triazine. Afterwards, the use of $\Delta_f H^\circ_{\text{Gas}}$ for 1,2,4-triazine, 1,3,5-triazine and 1,3-diazine values allow to calculate $\Delta_f H^\circ_{\text{Gas}}$ of 1,2,4,5-tetrazine. Secondly, using $\Delta_f H^\circ_{\text{Gas}}$ value of methylamine (CH$_3$NH$_2$), hydrazine (NH$_2$), and ammonia (NH$_3$) compounds, we have estimated the $\Delta_f H^\circ_{\text{Gas}}$ for 1,2-dimethyl-hydrazine (CH$_3$NH–NHCH$_3$).

Using the $\Delta_f H^\circ_{\text{Gas}}$ value of 1,2,4,5-tetrazine and 1,2-dimethyl-hydrazine molecules, we have calculated the $\Delta_f H^\circ_{\text{Gas}}$ for DHT, followed by the one for DiAT and DAAT. Finally, using the known $\Delta_f H^\circ_{\text{Gas}}$ values of azobenzene, azoxybenzene, pyridine and pyridine-N-oxide, the $\Delta_f H^\circ_{\text{Gas}}$ for the series of DAATO molecules at the gas phase were provided.

Regarding the case of DAATO molecule, it was mentioned in the literature that the DAATO in the condensed-phase contains an average of 3.2–3.6 oxygen atoms per molecule [9], which provides 13 possibilities for the positioning and quantity of oxygen atoms per molecule (Table 1).

The DAAT oxidation will preferably take place at N$_1$, N$'_1$, N$_3$, N$'_3$, N$_5$ and N$'_5$ positions rather than N$_2$, N$'_2$, N$_4$ and N$'_4$. The compound is more stable at N$_1$, N$'_1$, N$_3$ and N$'_3$ positions because of hydrogen bonds between oxygen and hydrogen of amine group. Indeed, Chavez and Hiskey [30] showed that the oxidation of 3-amino-1,2,4,5-tetrazine takes place at N$_1$ and N$_3$ positions. The DAATO molecule is presented by symbol DAATOn.j. Here n is the number of oxygen atoms by molecule (n = 1, 2, 3, 4, 5) and j is the isomer numbering.

The heat of formation in gas phase of molecules DAATO varies between 190.0 and 264.0 kcal/mol. These values decrease as the number of oxygen atoms in the molecule increases.

3.2. Heats of sublimation

In Table 2 are listed similar molecules to DHT, DAAT and DiAT which have been used to determine the three parameters β_{1-3} Eq. (2), using least-squares fitting needed according to Politzer approach in the estimation of heats of sublimation. The experimental values of heats of sublimation, ΔH_{Sub}, of molecules used for this fit are available [31]. The molecular surface area A, degree of

Table 1
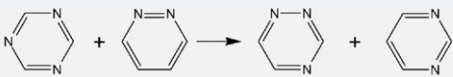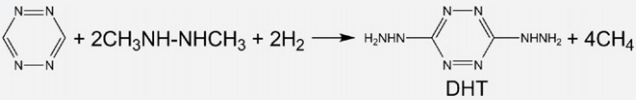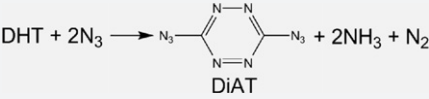Isodesmic reactions and predicted gas-phase heats of formation in kcal/mol.
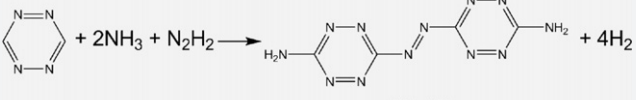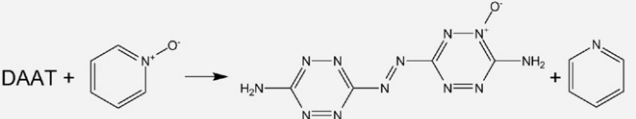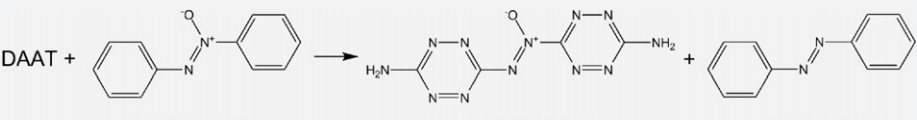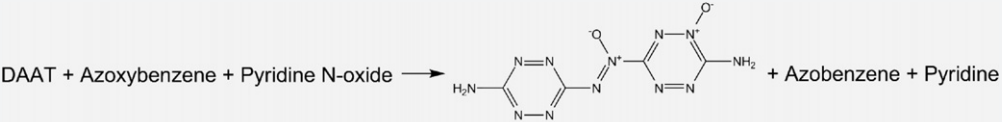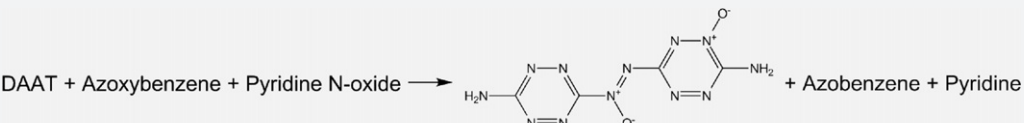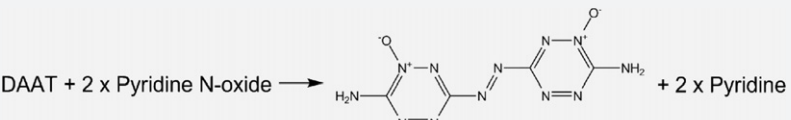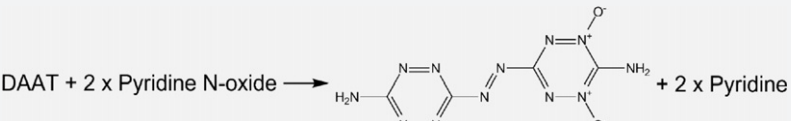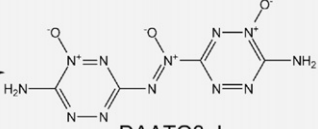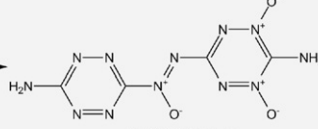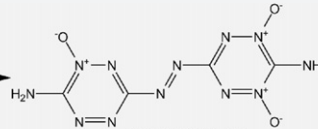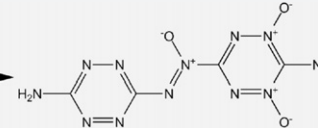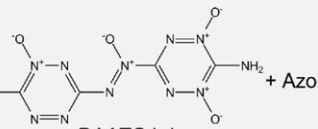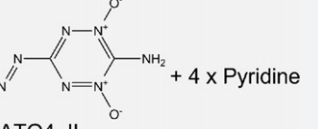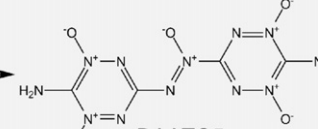
Molecules	Isodesmic reactions	$\Delta_f H^{\circ}_{Gas}$
1,2,4-Triazine	1,3,5-Triazine Pyridazine 1,2,4-Triazine 1,3-Diazine	78
1,2,4,5-Tetrazine	1,3,5-Triazine + 1,2,4-Triazine ⟶ + 1,3-Diazine 1,2,4,5-Tetrazine	111
1,2-Dimethyl-hydrazine	$2CH_3NH_2 + N_2H_4 \rightarrow CH_3NH-NHCH_3 + 2NH_3$	24
DHT	+ 2CH₃NH-NHCH₃ + 2H₂ ⟶ H₂NHN—⬡—NHNH₂ + 4CH₄ DHT	153
DiAT	DHT ⟶ N₃—⬡—N₃ + 2NH₃ + N₂ DiAT	257
DAAT	+ 2NH₃ + N₂H₂ ⟶ H₂N—⬡—N=N—⬡—NH₂ + 4H₂ DAAT	274
DAATO1_I	DAAT + ⟶ H₂N—⬡—N=N—⬡—NH₂ + Pyridine N-oxide DAATO1_I Pyridine	253
DAATO1_II	DAAT + ⟶ H₂N—⬡—N=N—⬡—NH₂ + Azoxybenzene DAATO1_II Azobenzene	264
DAATO2_I	DAAT + Azoxybenzene + Pyridine N-oxide ⟶ H₂N—⬡—N=N—⬡—NH₂ + Azobenzene + Pyridine DAATO2_I	243
DAATO2_II	DAAT + Azoxybenzene + Pyridine N-oxide ⟶ H₂N—⬡—N=N—⬡—NH₂ + Azobenzene + Pyridine DAATO2_II	240
DAATO2_III	DAAT + 2 x Pyridine N-oxide ⟶ H₂N—⬡—N=N—⬡—NH₂ + 2 x Pyridine DAATO2_III	231
DAATO2_IV	DAAT + 2 x Pyridine N-oxide ⟶ H₂N—⬡—N=N—⬡—NH₂ + 2 x Pyridine DAATO2_IV	236

Table 1 (*Continued*)

Molecules	Isodesmic reactions	$\Delta_f H^\circ_{\text{Gas}}$
DAATO3_I	DAAT + Azoxybenzene + 2 × Pyridine N-oxide ⟶ DAATO3_I + Azobenzene + 2 × Pyridine	221
DAATO3_II	DAAT + Azoxybenzene + 2 × Pyridine N-oxide ⟶ DAATO3_II + Azobenzene + 2 × Pyridine	226
DAATO3_III	DAAT + Azoxybenzene + 2 × Pyridine N-oxide ⟶ DAATO3_III + Azobenzene + 2 × Pyridine	223
DAATO3_IV	DAAT + Azoxybenzene + 2 × Pyridine N-oxide ⟶ DAATO3_IV + Azobenzene + 2 × Pyridine	227
DAATO4_I	DAAT + Azoxybenzene + 3 × Pyridine N-oxide ⟶ DAATO4_I + Azobenzene + 3 × Pyridine	205
DAATO4_II	DAAT + 4 × Pyridine N-oxide ⟶ DAATO4_II + 4 × Pyridine	199
DAATO5	DAAT + Azoxybenzene + 4 × Pyridine N-oxide ⟶ DAATO5 + Azobenzene + 4 × Pyridine	190

balance between negative and positive potential on the molecules surface ν and the square of the variability of the electrostatic potential on the molecular surface $(\sigma_{\text{total}})^2$ are listed in Table 2. In Table 3, the fit parameters $\beta_{1\text{-}3}$ are given and Table 4 shows the optimized structural parameters.

Using these parameters and calculated values for A, ν and $(\sigma_{\text{total}})^2$, a theoretical value of ΔH_{Sub} was calculated and the com-

Table 3
Regression coefficients $\beta_{1\text{-}3}$ for heats of sublimation.

Coefficients	Fitting dataset
β_1 (kcal/mol Å^4)	4×10^{-4}
β_2	2.2644
β_3 (kcal/mol)	0.2008

Table 2
B3LYP/6-311++G(3d,3p) molecular properties.

Name	A (Å^2)	ν	$(\sigma_{\text{total}})^2$ (kcal/mol)^2
5-Methyltetrazole	118.560	0.241	271.294
5-Amino-2-methyltetrazole	133.580	0.246	149.109
1,3,5-Triazine-2,4,6-triamine	177.000	0.229	150.381
1-Methyl-5-aminotetrazole	132.100	0.249	283.451
1-Methyltetrazole	120.110	0.245	203.604
Pyrazine	137.520	0.217	117.506
3-Aminopyridine	140.880	0.250	168.740
1-Methyl-1H-tetrazole	119.590	0.247	185.668
3,5-Dimethylpyrazole	153.760	0.228	158.634

Table 4
Experimental and calculated heats of sublimation ΔH_{Sub} in kcal/mol.
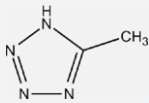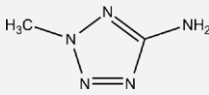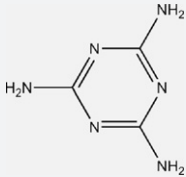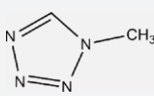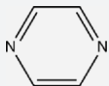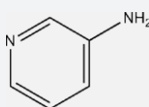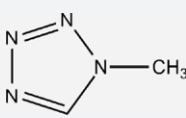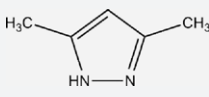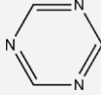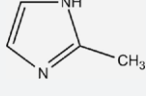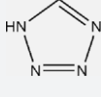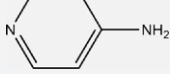
Name	Chemical structure	ΔH_{Sub} (Expt.)	ΔH_{Sub} (Theo.)	Diff.
5-Methyltetrazole		23.0	24.1	1.1
5-Amino-2-methyltetrazole		22.0	21.1	0.9
1,3,5-Triazine-2,4,6-triamine		28.7	26.1	2.6
1-Methyl-5-aminotetrazole		28.7	26.2	2.5
1-Methyltetrazole		21.1	22.0	0.9
Pyrazine		13.5	19.2	5.8
3-Aminopyridine		20.1	22.9	2.8
1-Methyl-1H-tetrazole		21.1	21.3	0.2
3,5-Dimethylpyrazole		19.9	23.3	3.4
1,3,5-Triazine		13.0	14.9	1.9
1H-Imidazole		19.8	24.3	4.5
2-Methyl-1H-imidazole		21.1	24.7	3.6
1H-Pyrazole		17.8	20.9	3.1
1H-Tetrazole		20.3	22.7	2.4
4-Aminopyridine		21.1	25.4	4.4

Table 5
Heats of sublimation in kcal/mol predicted using Politzer approach.

Name	A (Å^2)	ν	$(\sigma_{total})^2$ (kcal/mol)^2	ΔH_{Sub}
DHT	173.46	0.244	131.309	25
DiAT	179.40	0.248	120.934	26
DAAT	229.50	0.229	281.904	40

parison between the experimental and calculated values is given in Table 4 for each molecules used to perform the fit as well as some other molecules. As observed, the deviation between the experimental and theoretical values is about ±3.3 kcal/mol (RMS error). Good agreement observed between experimental and theoretical values as shown in Fig. 2. Finally, using the parameters obtained with the nine selected molecules, the ΔH_{Sub} of

DHT, DiAT and DAAT were calculated and the results are given in Table 5.

In the case of DAATO or oxygenated DAAT, the molecules of Table 6 were used to determine the values of three Politzer parameters β_{1-3} by least-squares fitting of equation (2). Again we selected molecules having structured similitude with DAATO and for which the experimental ΔH_{Sub} were available.

The best-fit parameters for Eq. (2) are given in Table 7, and the predicted heats of sublimation are given in Table 6 for comparison with the experimental information used in fitting. Fig. 3 shows the results of the fits for the heat of sublimation. The RMS error of the fit for these molecules is 2.5 kcal/mol. It is an acceptable error for the heat of sublimation prediction. The maximum deviation from experiment is 4.2 kcal/mol for hexahydro-1,3,5-trinitroso-1,3,5-triazine.

Table 6
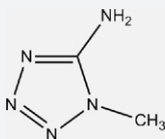Experimental and calculated heats of sublimation ΔH_{Sub} in kcal/mol.

Name	Chemical structure	A (Å^2)	ν	$(\sigma_{total})^2$ (kcal/mol)^2	ΔH_{Sub} (Expt.)	ΔH_{Sub} (Theo.)	Diff.
5-Methyl-3-isoxazolamine		140.54	0.229	185.940	19.6	21.08	1.48
2-Imidazolidinone		140.04	0.153	246.961	20.00	20.20	0.19
RDX		200.23	0.181	149.695	26.77	24.17	2.60
Hexahydro-1,3,5-trinitroso-1,3,5-triazine		180.47	0.217	144.000	27.01	22.81	4.20
TNT		219.64	0.208	100.822	25.00	25.20	0.20
1,3,5-Trinitrobenzene		210.77	0.183	117.853	23.80	24.19	0.39
1,4-Dinitroso-piperazine		166.97	0.238	117.289	24.14	20.69	3.45
Azoxybenzene		237.90	0.247	58.217	23.57	25.92	2.36
Pyridine-N-oxide		152.42	0.160	303.909	19.57	23.17	3.59

Fig. 2. Calculated heats of sublimation versus experimental values for 19 parameterization molecules. The solid line represents perfect agreement.

Table 7
Regression coefficients β_{1-3} for heats of sublimation.

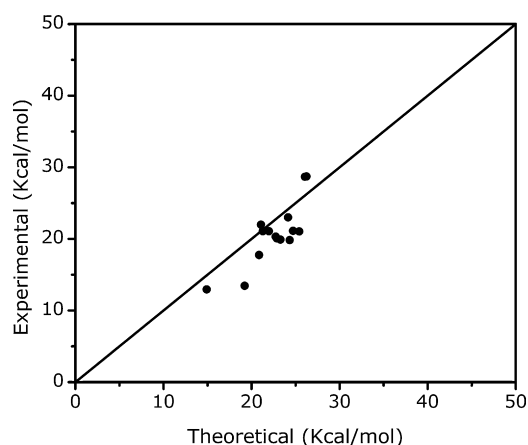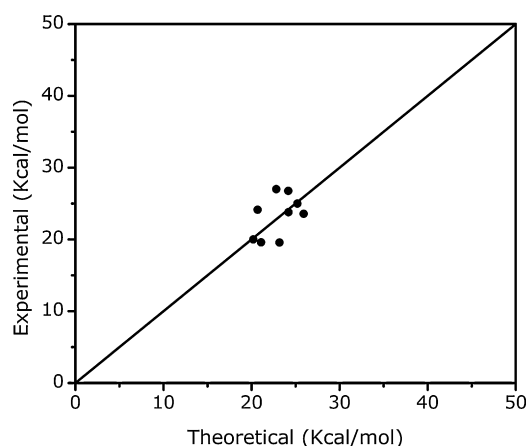| Coefficient	Fitting dataset
β_1 (kcal/mol Å^4)	3×10^{-4}
β_2	2.2765
β_3 (kcal/mol)	0.2921

Fig. 3. Calculated heats of sublimation versus experimental values for nine parameterization molecules. The solid line represents perfect agreement.

All results of heats of sublimation for DAATO molecules are listed in Table 8. It should be noted that the values of heat of sublimation for a given isomer are quite the same; an average value is proposed for each molecule with the number of oxygen atoms in the oxygenated DAAT.

3.3. Condensed-phase heats of formation

The estimated heats of formation at the solid phase $\Delta_f H^\circ_{\text{Solid}}$ are given in Table 9. From the results we note that all 16

Table 8
Heats of sublimation predicted by Politzer in kcal/mol.

Name	A (Å^2)	ν	$(\sigma_{\text{total}})^2$ (kcal/mol)^2	$\Delta_f H^\circ_{\text{Sub}}$
DAATO1	239.76	0.2242	268.567	35
DAATO2	246.09	0.2036	258.341	35
DAATO3	253.56	0.1971	251.857	36
DAATO4	264.02	0.1929	245.549	37
DAATO4	263.58	0.1959	247.118	37
DAATO5	274.26	0.1857	232.959	38

Table 9
Predicted condensed-phase heats of formation, detonation velocity (D) and detonation pressure (P) for DHT, DiAT, DAAT and DAATO.

Molecule	$\Delta_f H^\circ_{\text{Solid}}$ (kcal/mol)	D (m/s)	P (GPa)
DHT	128 (128)[a]	8319	30.41
DiAT	231	9068	36.77
DAAT	234 (206 or 247)[b]	8250	31.14
DAATO1_I	218	8745	37.38
DAATO1_II	229	8768	37.57
DAATO2_I	208	8902	38.73
DAATO2_II	205	8881	38.55
DAATO2_III	196	8876	38.51
DAATO2_IV	201	8907	38.78
DAATO3_I	185	9015	39.72
DAATO3_II	190	9039	39.94
DAATO3_III	187	9020	39.77
DAATO3_IV	191	9044	39.98
DAATO4_I	168	9147	40.90
DAATO4_II	162	9156	40.98
DAATO5	152	9266	41.96

[a] Experimental values: Ref. [12].
[b] Experimental values: Ref. [13].

molecules studied have indeed high positive heats of formation, which are comparable to, for example, 3,6-bis(2H-tetrazol-5-yl)-1,2,4,5-tetrazine (BTT) (223 kcal/mol) [32] and other high-nitrogen compounds discussed in Refs. [5,33].

In Table 9, experimental values $\Delta_f H^\circ_{\text{Solid}}$ were reported for DHT and DAAT. For DHT both values, experimental and predict, are identical. For DAAT the calculated value is between two experimental values reported in the literature, the relative error is from 5 to 14%.

The trends within the given set of molecules are similar between the gas-phase and condensed-phase results, with the highest heat of formation reached by DiAT compound ($\Delta_f H^\circ_{\text{Solid}} = 231$ kcal/mol), presumably because of the presence of azide group N_3 [10].

Regarding DAATO molecules, the condensed-phase heats of formation decreases when the number of oxygen increases, which can be understood by the relationship between heat of formation and reaction, the latter is low when the number of oxygen atom increases because the molecule uses its oxygen atoms in the combustion process. The condensed-phase heats of formation vary between 152 and 229 kcal/mol. Since it was discussed in Ref. [9] that the DAATO compound contains 3.2–3.6 oxygen atoms per molecule. This means that DAATO molecule could be composed with various DAATO molecules involving various numbers of oxygen atoms from
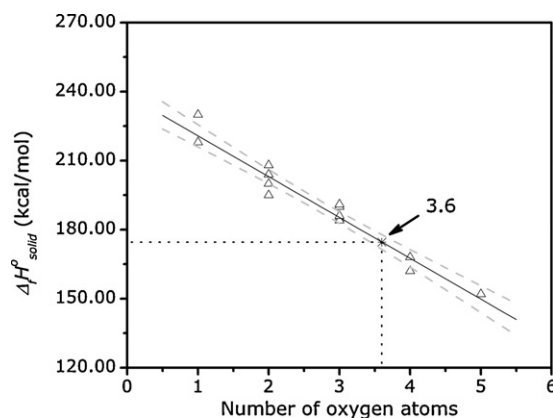

Fig. 4. Heat of formation at condensation phase of DAATO compound as a function of number of oxygen atoms. Lines represent linear regression results and dashed lines represent upper and lower 95% confidence limit.

Fig. 5. Detonation velocity (D) and detonation pressure (P) of DAATO compound as a function of number of oxygen atoms. Lines represent linear regression results and dashed lines represent upper and lower 95% confidence limit.
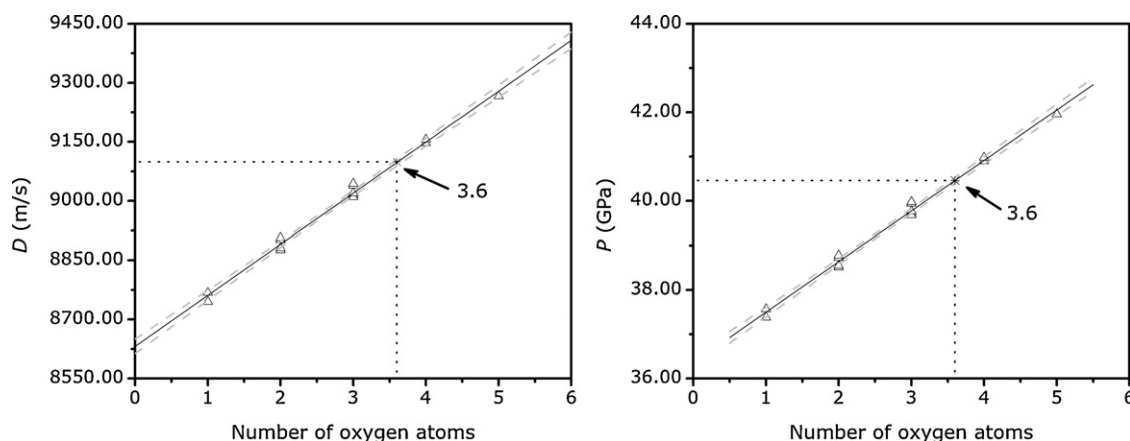
1 to 5. Fig. 4 shows the heat of formation of all DAATO molecules as a function of the number of oxygen atoms. The heat of formation at condensed phase of DAATO with 3.6 oxygen atoms was estimated at 174.59 ± 3.18 kcal/mol using linear regression method. The linear regression method was used as an approach for predicted heats of formation values of DAATO molecules which contain 1–5 oxygen atoms in order to estimate the heat of formation of DAATO3.6 molecule. Confidence intervals were calculated using the Origin 6.1 Software at a 95% probability level and used to estimate the error associated to $\Delta_f H^{\circ}_{Solid}$ values predicted by this method.

3.4. Detonation properties

For any explosive, the detonation velocity (D), and detonation pressure (P) are the most important factors to assess its performance. Up to now, many theoretical or empirical methods have been suggested to predict detonation properties [34–37]. In this work, the Stine method was selected to estimate the detonation velocity D (m/s) [36] and detonation pressure P (GPa) [38] are given by following expressions:

$$D = D_0 + \frac{\rho[c_1 n_C + c_2 n_N + c_3 n_O + c_4 n_H + c_5 \ \Delta_f H^{\circ}_{Solid}]}{M} \quad (3)$$

$$P = 0.26 \rho D^2 \quad (4)$$

where ρ is the density (g/cm^3) of the molecular system, M is the molecular mass, D_0 and c_i ($i = 1, 2, 3, 4, 5$) are the characteristic velocity of the void assumed to equal to 3.69 km/s and coefficients respectively. The coefficients c_i ($c_1 = -13.85$, $c_2 = 37.74$, $c_3 = 68.11$, $c_4 = 3.95$ and $c_5 = 0.1653$) are provided using the least-square sense technique [30], $\Delta_f H^{\circ}_{Solid}$ is in kJ/mol and n_C; n_N; n_O, and n_H are numbers of C, N, O, and H atoms present in the molecule, respectively. The experimental data of the density of DHT, DiAT, DAAT and DAATO molecules are 1.69 g/cm^3 [12], 1.72 g/cm^3 [39], 1.76 g/cm^3 [13] and 1.88 g/cm^3 [9], respectively according some references.

Table 9 gives the results obtained using Eqs. (3) and (4) for the molecules studied in this work. From Table 9, the detonation velocity values for our molecules range from 8745 to 9266 m/s, showing that from detonation performance aspect DiAT and DAATO_i ($i = 1$, 2, 3, 4, 5) are best candidates in comparison to conventional energetic compounds such as RDX, and TNT (6900 and 8750 m/s, respectively). Fig. 5 shows the behaviour of the detonation velocity and pressure as a function of number of oxygen atoms in oxygenated DAAT molecules, respectively. It is clear that DiAT seems to be the best candidate in these series of molecules stud-

ied. However, some oxygenated DAAT molecules arise with a high detonation velocity and pressure, similar analysis could be done regarding these physical properties determining an average value for $D = 9098.92 \pm 8.04$ m/s and $P = 40.46 \pm 0.07$ GPa with 95% as a confidence interval, these values correspond to DAATO product with a ratio of 3.6 oxygen atoms in the final product.

4. Conclusions

In summary, using first-principles calculations at the DFT level we have studied the physical properties of several molecules as nitrogen-rich energetic compounds. Based on specially designed sets of isodesmic reactions, standard gas-phase heats of formations are predicted. We also provide estimates of the condensed-phase heats of formation, in the framework of the Politzer model. From those results, we found that the B3LYP/6-311++G(3d,3p) method provides a good estimation for enthalpies, in comparison with experimental data available for DHT and DAAT compounds. DiAT molecule as a high-nitrogen compound because of the azide group N$_3$, is a very promising molecule as a potential advanced energetic materials for the next generation. This molecule has the highest heat of formation and good physical properties. Regarding the oxygenated DAAT molecules, from the theoretical assessment we observe that their heats of formation are estimated in the range of 152.0–229.0 kcal/mol. The highest heat of formation value corresponds to DAATO1_II isomer with one oxygen atom. However, DAATO with five oxygen atoms is characterized with high physical properties. From this theoretical point of view DAATO is probably a combination of various possibilities of oxygenated DAAT molecules as it was already confirmed experimentally. From the predicted results these oxygenated DAAT molecules; we should consider an average value of all heats of formation at the solid phase as well as for physical properties. Synthetic work for all molecules investigated in this work is in progress and measurements of heats of formation, and sensitivity properties respect to the impact and friction will also be performed. The use of various experimental techniques will offer the possibility to quantify each oxygenated DAAT molecule composing the final product that gives a ratio around 3.6 oxygen atoms per DAATO molecule.

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