

# Thermochemical studies of two *N*-(diethylaminothiocarbonyl)benzimidido derivatives

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## Abstract

The standard ( $p^\circ = 0.1$  MPa) molar energies of combustion in oxygen of *N*-(diethylaminothiocarbonyl)-*N'*-monoethylbenzamidine, PhCNHEtNCSNEt<sub>2</sub> (DATMB), and *N*-(diethylaminothiocarbonyl)benzimidido ethylester, PhCOEtNCSNEt<sub>2</sub> (DATBE), were measured, at  $T = 298.15$  K, by rotating-bomb calorimetry. The standard molar enthalpies of sublimation of these compounds were determined using Calvet microcalorimetry. These values were used to derive the standard molar enthalpies of formation of the title compounds, in their crystalline and gaseous phases, respectively.

Compounds	$-\Delta_c U_m^\circ(\text{cr}) /$ (kJ · mol <sup>-1</sup> )	$-\Delta_f H_m^\circ(\text{cr}) /$ (kJ · mol <sup>-1</sup> )	$\Delta_{\text{cr}}^g H_m^\circ /$ (kJ · mol <sup>-1</sup> )
<i>N</i> -(Diethylaminothiocarbonyl)- <i>N'</i> -monoethylbenzamidine (DATMB)	9053.6 ± 3.9	45.7 ± 4.4	141.2 ± 1.2
<i>N</i> -(Diethylaminothiocarbonyl)benzimidido ethylester (DATBE)	8780.9 ± 4.0	176.2 ± 4.4	135.6 ± 2.6

The standard molar enthalpies of formation for the two title compounds, in the gaseous state, were also calculated based on density functional theory at the B3LYP/6-311++G(2df,p)//6-31+G(d,p)-level of theory, anchored on previous experimental data for the standard molar enthalpy of formation of *N*-(diethylaminothiocarbonyl)-benzamidine.

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**Keywords:** Enthalpy of combustion; Enthalpy of sublimation; Enthalpy of formation; *N*-Thiocarbamoylbenzamidines; Benzimidido derivatives of thioureas; *N*-(Diethylaminothio-carbonyl)-*N'*-monoethylbenzamidine; *N*-(Diethylaminothiocarbonyl)benzimidido ethylester

## 1. Introduction

*N*-Thiocarbamoylbenzamidines are potentially bidentate ligands, with the ability for complex formation towards transition metal ions [1,2]. These compounds have been investigated due to their application as radiopharmaceuticals (<sup>99m</sup>Tc) [3]. Benzamidines and a variety of their derivatives are known starting materials for a large number of Serine proteinase inhibitors [4–6]. Bridged *N*-thiocarbamoyl substituted bis-benzamidines Et<sub>2</sub>NCSNCPH–NH–R–

NH–CPhNCSNEt<sub>2</sub>, with different moieties R, and their respective transition metal complexes have been reported [7]. Recently, we reported on thermochemical studies on *N*-thiocarbamoylbenzamidines [8] as well as on their respective Ni(II) complexes [9]. Following these previous investigations, the aim of this work is to link and to extent the scope of compounds to the more general class of benzimidido derivatives of thioureas, and, further, study their energetics in order to contribute to the understanding of binding processes, *e.g.*, in biologically relevant materials.

In the present work, we report on the thermochemistry of *N*-(diethylaminothiocarbonyl)-*N'*-monoethylbenzamidine (DATMB) and *N*-(diethylaminothiocarbonyl)benzimidido ethylester (DATBE), as shown in figure 1: the standard

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molar enthalpies of formation of the crystalline compounds, at  $T = 298.15$  K, were obtained from measurements of their energies of combustion in a rotating-bomb calorimeter, their standard molar enthalpies of sublimation were determined by Calvet microcalorimetry and the standard molar enthalpies of formation for the corresponding compounds, in the gaseous state, at  $T = 298.15$  K, were derived.

The standard molar enthalpies of formation for the two title compounds, in the gaseous state, were also calculated based on density functional theory at the B3LYP/6-311++G(2df,p)//6-31+G(d,p)-level of theory, anchored on previous experimental data for the standard molar enthalpy of formation of *N*-(diethylaminothiocarbonyl)-benzimidine (DATB:  $\text{PhC}(\text{NH}_2)\text{NCSN}(\text{Et})_2$ ) [8].

## 2. Experimental

### 2.1. Synthesis and characterization

The substitution of chlorine in the precursor *N*-(diethylaminothiocarbonyl)benzimidate chloride (see figure 2), which is available through the reaction of equimolar amounts of bis(*N,N'*-diethyl-*N*-benzoylthiourea)nickel(II) and thionyl chloride in dried THF, yielded the title compounds.

*N*-(diethylaminothiocarbonyl)-*N'*-monoethylbenzimidine (DATMB): pure *N*-(diethylaminothiocarbonyl)benzimidate chloride reacts with monoethyl amine in acetone. In the presence of a proton-catching reagent (triethylamine) and after removing the precipitating triethylamine hydrochloride and successful recrystallisation from ethanol, the respective *N*-thiocarbamoyl-benzimidine (DATMB), has been obtained in pale, yellow crystals [1].

*N*-(diethylaminothiocarbonyl)benzimidate ethylester (DATBE): equimolar amounts of sodium ethanoate (readily available

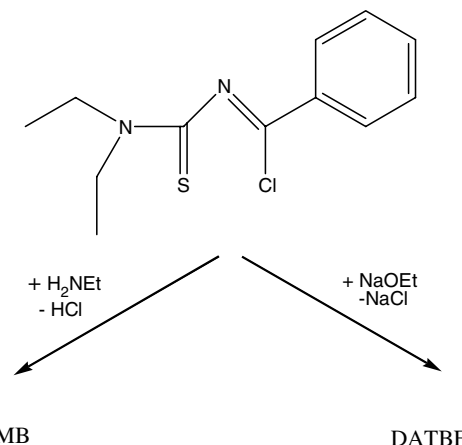


FIGURE 2. The substitution of chlorine in *N*-(diethylaminothiocarbonyl)benzimidate chloride yielded the thiourea derived title compounds [1].

from refluxing ethanol over sodium under a nitrogen atmosphere) and *N*-(diethylaminothiocarbonyl)benzimidate chloride were dissolved in ethanol. After refluxing and removing the solvent in vacuum, the residue is taken over with 20 cm<sup>3</sup> of H<sub>2</sub>O; the precipitating oil crystallizes after applying some friction. The pale yellow crystals of DATBE were washed with water and recrystallized from *n*-hexane [1].

The purity of the samples was checked by IR spectroscopy and by elemental analysis; the mass fraction  $w$  of C, H, N and S were as follows: for DATMB,  $\text{C}_{14}\text{H}_{21}\text{N}_3\text{S}$ , found  $10^2w(\text{C}) = 63.6$ ,  $10^2w(\text{H}) = 8.9$ ,  $10^2w(\text{N}) = 15.9$ ,  $10^2w(\text{S}) = 12.0$ , calculated  $10^2w(\text{C}) = 63.84$ ,  $10^2w(\text{H}) = 8.04$ ,  $10^2w(\text{N}) = 15.95$ ,  $10^2w(\text{S}) = 12.17$ ; for DATBE,  $\text{C}_{14}\text{H}_{20}\text{N}_2\text{OS}$ , found  $10^2w(\text{C}) = 63.5$ ,  $10^2w(\text{H}) = 7.8$ ,  $10^2w(\text{N}) = 10.3$ ,  $10^2w(\text{O}) = 6.0$ ,  $10^2w(\text{S}) = 12.0$ , calculated  $10^2w(\text{C}) = 63.60$ ,  $10^2w(\text{H}) = 7.62$ ,  $10^2w(\text{N}) = 10.60$ ,  $10^2w(\text{O}) = 6.05$ ,  $10^2w(\text{S}) = 12.13$ .

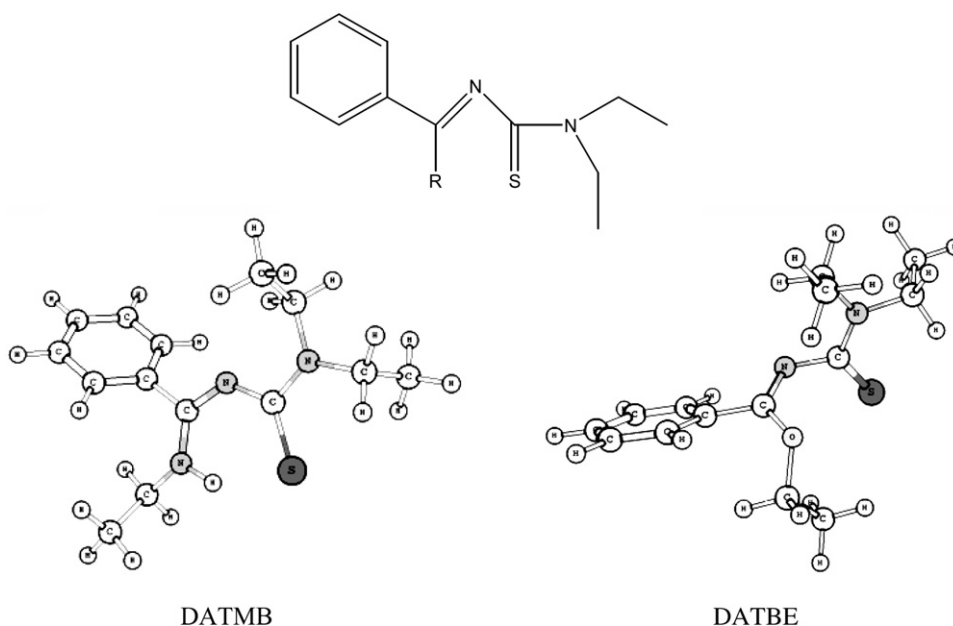


FIGURE 1. General formula of the two *N*-(diethylaminothiocarbonyl)benzimidate derivatives. R-NHEt: *N*-(diethylaminothiocarbonyl)-*N'*-monoethylbenzimidine (DATMB); R-OEt: *N*-(diethylaminothiocarbonyl)benzimidate ethylester (DATBE).

The relative atomic masses used were those recommended by the IUPAC Commission in 2001 [10].

## 2.2. Combustion calorimetry

The enthalpies of combustion were measured with the rotating-bomb calorimeter formerly used at the National Physical Laboratory, Teddington, UK [11], with a tantalum-lined bomb of internal volume 0.329 dm<sup>3</sup> and a tantalum head. Water was added to the calorimeter from a weighed acrylic vessel, and for each experiment a correction to the energy equivalent was made for the deviation from 3965.0 g of the mass of water added. Calorimetric temperatures were measured to  $1 \cdot 10^{-4}$  K with a quartz thermometer (Hewlett–Packard HP 2804A) interfaced to a microcomputer programmed to compute the adiabatic temperature change. Ignition temperatures were chosen so that the final temperatures were very close to 298.15 K. The frictional work of bomb rotation and stirring was automatically included in the correction for heat exchange by using the procedure described by Good *et al.* [12]. Data acquisition and control of the calorimeter were performed using the program LABTERMO [13].

The energy equivalent of the calorimeter was determined from the combustion of benzoic acid (NBS Standard Reference Material 39i), having a massic energy of combustion under bomb conditions of  $-(26434 \pm 3) \text{ J} \cdot \text{g}^{-1}$ , as previously described [14]. The electrical energy for the ignition was determined from the change in potential across a capacitor when 40 V were discharged through a platinum ignition wire. For the cotton thread fuse (empirical formula  $\text{CH}_{1.686}\text{O}_{0.843}$ ) the massic energy of combustion is assigned as  $\Delta_c u^\circ = -16240 \text{ J} \cdot \text{g}^{-1}$  [12], a value that has been confirmed in our laboratory. Corrections for nitric acid formation were based on  $-59.7 \text{ kJ} \cdot \text{mol}^{-1}$  for the molar energy of formation of  $0.1 \text{ mol} \cdot \text{dm}^{-3}$   $\text{HNO}_3(\text{aq})$  from  $\text{O}_2$ ,  $\text{N}_2$ , and  $\text{H}_2\text{O}(\text{l})$  [15].

From 10 calibration experiments, the energy equivalent of the calorimeter,  $\varepsilon(\text{calor})/(\text{J} \cdot \text{K}^{-1})$  was found to be  $\{20369.0 \pm 2.3 (0.011\%)\}$ , for an average mass of water added to the calorimeter of 3965.0 g; the quoted uncertainty refers to the standard deviation of the mean.

Samples in pellet form were ignited in oxygen at a pressure of 3.04 MPa with a volume of 5 cm<sup>3</sup> of water added to the bomb. The amount of nitric acid was determined using ion chromatography. The densities of the title compounds were assumed to be  $1.3 \text{ g} \cdot \text{cm}^{-3}$ . For each compound,  $(\partial u / \partial p)_T$ , at  $T = 298.15 \text{ K}$ , was assumed to be  $-0.2 \text{ J} \cdot \text{g}^{-1} \cdot \text{MPa}^{-1}$ , a typical value for most organic compounds. Standard state corrections were calculated for the initial states by the procedures given by Hubbard *et al.* [16] and by Good and Scott [17].

## 2.3. Calvet microcalorimetry

The standard molar enthalpies of sublimation have been measured using the Calvet microcalorimetry drop-method

[18,19]. Samples of about 5 mg of each compound, contained in thin glass capillary tubes sealed at one end, were dropped from room temperature into the hot reaction vessel in the Calvet High Temperature Microcalorimeter (Setaram HT 1000D), held at  $T = 416.8 \text{ K}$  (DATMB), or at  $T = 401.3 \text{ K}$  (DATBE) and then removed from the hot zone by vacuum sublimation. The observed standard molar enthalpies of sublimation  $\Delta_{\text{cr},298.15 \text{ K}}^{\text{g},T} H_{\text{m}}^\circ$  have been corrected to  $T = 298.15 \text{ K}$  using  $\Delta_{298.15 \text{ K}}^T H_{\text{m}}^\circ(\text{g})$  calculated from the harmonic vibrational frequencies at the B3LYP/6-31+G(d,p) applying a scale factor of 0.9613: for  $\text{PhC}(\text{NHEt})\text{NCSN}(\text{Et})_2$ , at  $T = 416.8 \text{ K}$ ,  $\Delta_{298.15 \text{ K}}^{T=416.8 \text{ K}} H_{\text{m}}^\circ(\text{DATMB}, \text{g}) = 44.0 \text{ kJ} \cdot \text{mol}^{-1}$  and, for  $\text{PhC}(\text{NHEt})\text{NCSN}(\text{Et})_2$ , at  $T = 401.3 \text{ K}$ ,  $\Delta_{298.15 \text{ K}}^{T=401.3 \text{ K}} H_{\text{m}}^\circ(\text{DATBE}, \text{g}) = 36.4 \text{ kJ} \cdot \text{mol}^{-1}$ .

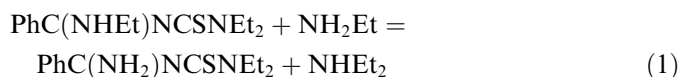
The calorimeter was calibrated *in situ*, making use of the reported standard molar enthalpy of sublimation of naphthalene,  $\text{C}_{10}\text{H}_8$ ,  $\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^\circ = (72.600 \pm 0.600) \text{ kJ} \cdot \text{mol}^{-1}$  [20], at  $T = 298.15 \text{ K}$ . The calibration constant of the calorimeter was obtained as the average of six independent experiments at  $T = 416.8 \text{ K}$  as  $K = (0.9832 \pm 0.0079)$ . The temperature was measured *in situ* using a small size Pt100 probe previously calibrated against a SPRT Tinsley (25  $\Omega$ ; Model 5187SA) probe. Thermal corrections for the glass capillaries were made by dropping tubes of near equal mass into each of the twin cells [19].

## 3. Computational thermochemistry details

For all involved species, full geometry optimizations with Becke's three-parameter exchange functional [21] in combination with the Lee, Yang and Parr correlation function as hybrid exchange-correlation energy functional (B3LYP) [22] at a 6-31+G(d,p)-level of theory, were performed first, to yield the most stable geometries, and B3LYP single-point energies were obtained with the 6-311++G(2df,p) basis set. The zero-point energies ( $\varepsilon_{\text{ZPE}}$ ) are scaled to 0.9804 [23]. Harmonic vibrational frequencies were calculated at the 6-31+G(d,p)-level of theory, applying a scaling factor 0.9613 for the correction of anharmonicity [23], using the implementation of DFT in the Gaussian-03 suite of programs [24].

The standard molar enthalpies of formation of the two title compounds, in the gaseous state, were derived based on the following hypothetical group exchange reactions, anchored on the experimental data for the standard molar enthalpy of formation of *N*-(diethylaminothiocarbonyl)-benzamidine (DATB:  $\text{PhC}(\text{NH}_2)\text{NCSN}(\text{Et})_2$ ) [8], in the gaseous state:

For DATMB,



and for DATBE,

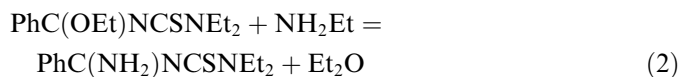


TABLE 1

Total energies in  $\text{kJ} \cdot \text{mol}^{-1}$  of the reactants of the empirical group exchange reactions

Energy	DATMB	DATBE	$\text{NH}_2\text{Et}$	$\text{NHEt}_2$	$\text{Et}_2\text{O}$	DATB
$\varepsilon_{\text{ZPE}}(6\text{-}31+\text{G}(\text{d,p}))$	859.35	825.82	238.42	383.06	351.32	859.35
$\varepsilon_0(6\text{-}311++\text{G}(2\text{df,p})//6\text{-}31+\text{G}(\text{d,p}))$	−2911304.27	−2963441.37	−355036.50	−561505.37	−613690.03	−2911304.27
$\varepsilon_{\text{H}}(6\text{-}311++\text{G}(2\text{df,p})//6\text{-}31+\text{G}(\text{d,p}))$	−2910390.23	−2962562.85	−354783.74	−561103.22	−613317.97	−2910390.23

Full geometry optimizations with the B3LYP functional at a 6-31+G(d,p)-level of theory were performed first, followed by frequency calculations at the same level of theory. Single point calculations B3LYP using the previous optimized geometries 6-311++G(2df,p)//6-31+G(d,p). DATMB: *N*-(diethylaminothiocarbonyl)-*N'*-monoethylbenzamidine, DATBE: *N*-(diethylaminothiocarbonyl)benzimidio ethylester,  $\text{NH}_2\text{Et}$ : ethylamine,  $\text{NHEt}_2$ : diethylamine,  $\text{Et}_2\text{O}$ : diethyl ether, and DATB: *N*-(diethylaminothiocarbonyl)-benzamidine.

Assigned energy corrections to the total energy ( $\text{kJ} \cdot \text{mol}^{-1}$ ):  $\varepsilon_{\text{ZPE}}$ , zero-point correction;  $\varepsilon_0$ , total electronic energy;  $\varepsilon_{\text{H}}$  = total electronic energy + zero-point energy (scaled to 0.9804) + enthalpy correction (scaled to 0.9613).

Table 1 lists the obtained total energies and enthalpies, at  $T = 298.15 \text{ K}$ , of the species involved in the previous reactions.

To derive  $\Delta_f H_m^\circ(\text{g})$  from the B3LYP results, the following experimental data for the standard molar enthalpy of formation in gas phase, at  $T = 298.15 \text{ K}$ , were used:  $\Delta_f H_m^\circ(\text{NH}_2\text{Et}, \text{g}) = -(47.5 \pm 0.6) \text{ kJ} \cdot \text{mol}^{-1}$  [25];  $\Delta_f H_m^\circ(\text{NHEt}_2, \text{g}) = -(72.7 \pm 1.2) \text{ kJ} \cdot \text{mol}^{-1}$  [25];  $\Delta_f H_m^\circ(\text{Et}_2\text{O}, \text{g}) = -(252.2 \pm 0.79) \text{ kJ} \cdot \text{mol}^{-1}$  [26]; *N*-(diethylaminothiocarbonyl)-benzamidine, DATB:  $\Delta_f H_m^\circ[\text{PhC}(\text{NH}_2)\text{-NCSNEt}_2, \text{g}] = (124.6 \pm 4.1) \text{ kJ} \cdot \text{mol}^{-1}$  [8].

#### 4. Results

Table 2 lists typical combustion results for each compound in which  $\Delta m(\text{H}_2\text{O})$  is the deviation of the mass of water added to the calorimeter from 3965.0 g, the mass assigned to  $\varepsilon$  (calor), and  $\Delta U_\Sigma$  is the correction to the standard state. The remaining quantities are as previously described [16].

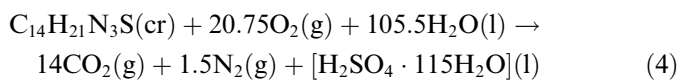
The internal energy for the isothermal bomb process,  $\Delta U(\text{IBP})$ , was calculated according to the following equation:

$$\Delta U(\text{IBP}) = -\{\varepsilon(\text{calor}) + c_p(\text{H}_2\text{O}, \text{l})\Delta m(\text{H}_2\text{O})\}\Delta T_{\text{ad}} + (T_i - 298.15)\varepsilon_i + (298.15 - T_i + \Delta T_{\text{ad}})\varepsilon_f + \Delta U(\text{ign}), \quad (3)$$

where  $\Delta T_{\text{ad}}$  is the calorimeter temperature change corrected for the heat exchange and the work of stirring.

For each compound, the products of combustion in the experiments consist of a gaseous phase and an aqueous mixture of sulphuric acid for which the thermodynamic properties are known. The values of  $\Delta_c u^\circ$  refer to the reactions represented by equations (4) and (5), for DATMB and DATBE, respectively:

DATMB:



DATBE:

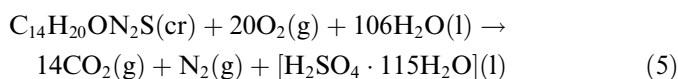


TABLE 2

Typical experimental results for the combustion of *N*-(diethylaminothiocarbonyl)-*N'*-monoethylbenzamidine (DATMB) and *N*-(diethylaminothiocarbonyl)benzimidio ethylester (DATBE), at  $T = 298.15 \text{ K}$

	DATMB	DATBE
$m(\text{cpd})/\text{g}$	0.61837	0.64249
$m'(\text{fuse})/\text{g}$	0.00364	0.00318
$T_i/\text{K}$	297.2665	297.1474
$T_f/\text{K}$	298.3246	298.2105
$\Delta T_{\text{ad}}/\text{K}$	1.03426	1.03531
$\varepsilon_i(\text{cont})/(\text{J} \cdot \text{K}^{-1})$	32.6	32.6
$\varepsilon_f(\text{cont})/(\text{J} \cdot \text{K}^{-1})$	32.5	32.4
$\Delta m(\text{H}_2\text{O})/\text{g}$	66.5	75.9
$-\Delta U(\text{IBP})/\text{J}$	21387.1	21449.5
$\Delta U(\text{HNO}_3)/\text{J}$	54.4	46.4
$\Delta U(\text{ignition})/\text{J}$	1.2	1.2
$\Delta U_\Sigma/\text{J}$	15.2	14.9
$m' \cdot \Delta_c u^\circ(\text{fuse})/\text{J}$	59.1	51.6
$-\Delta_c u^\circ(\text{cpd})/(\text{J} \cdot \text{g}^{-1})$	34378.1	33209.2

$m(\text{cpd})$  is the mass of compound burnt in each experiment;  $m'(\text{fuse})$  is the mass of the fuse (cotton) used in each experiment;  $T_i$  is the initial temperature rise;  $T_f$  is the final temperature rise;  $\Delta T_{\text{ad}}$  is the corrected temperature rise;  $\varepsilon_i(\text{cont})$  is the energy equivalent of the contents in the initial state;  $\varepsilon_f(\text{cont})$  is the energy equivalent of the contents in the final state;  $\Delta m(\text{H}_2\text{O})$  is the deviation of mass of water added to the calorimeter from 3965.0 g;  $\Delta U(\text{IBP})$  is the energy change for the isothermal combustion reaction under actual bomb conditions;  $\Delta U(\text{HNO}_3)$  is the energy correction for the nitric acid formation;  $\Delta U(\text{ignition})$  is the electric energy for the ignition;  $\Delta U_\Sigma$  is the standard state correction;  $\Delta_c u^\circ(\text{fuse})$  is the massic energy of combustion of the fuse (cotton);  $\Delta_c u^\circ$  is the standard massic energy of combustion.

<sup>a</sup>  $\Delta U(\text{IBP})$  includes  $\Delta U(\text{ignition})$ .

TABLE 3

Individual values of the standard ( $p^\circ = 0.1 \text{ MPa}$ ) massic energy of combustion,  $\Delta_c u^\circ$ , of *N*-(diethylaminothiocarbonyl)-*N'*-monoethylbenzamidine (DATMB), and *N*-(diethylaminothiocarbonyl)benzimidio ethylester (DATBE), at  $T = 298.15 \text{ K}$

DATMB	DATBE
$-\Delta_c u^\circ/(\text{J} \cdot \text{g}^{-1})$	
34378.1	33209.2
34367.0	33232.8
34372.4	33218.2
34358.8	33204.0
34360.0	33194.6
34391.6	33211.5
$-\langle \Delta_c u^\circ \rangle/(\text{J} \cdot \text{g}^{-1})^a$	
$34371.3 \pm 5.0$	$33211.7 \pm 5.3$

<sup>a</sup> Mean value; uncertainty is the standard deviation of the mean.



TABLE 4

Derived standard ( $p^\circ = 0.1$  MPa) molar energies of combustion,  $\Delta_c U_m^\circ$ , standard molar enthalpies of combustion,  $\Delta_c H_m^\circ$ , standard molar enthalpies of formation,  $\Delta_f H_m^\circ$ , and standard molar enthalpies of sublimation,  $\Delta_{cr}^\circ H_m^\circ$ , of *N*-(diethylaminothiocarbonyl)-*N'*-monoethylbenzamidine (DATMB), and *N*-(diethylaminothiocarbonyl)benzimidazole ethylester (DATBE), at  $T = 298.15$  K

	$-\Delta_c U_m^\circ(\text{cr})/(\text{kJ} \cdot \text{mol}^{-1})$	$-\Delta_c H_m^\circ(\text{cr})/(\text{kJ} \cdot \text{mol}^{-1})$	$-\Delta_f H_m^\circ(\text{cr})/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_{cr}^\circ H_m^\circ/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_f H_m^\circ(\text{g})/(\text{kJ} \cdot \text{mol}^{-1})$
DATMB	$9053.6 \pm 3.9$	$9066.6 \pm 3.9$	$45.7 \pm 4.4$	$141.2 \pm 1.2$	$95.5 \pm 4.6$
DATBE	$8780.9 \pm 4.0$	$8793.3 \pm 4.0$	$176.2 \pm 4.4$	$135.6 \pm 2.6$	$-40.6 \pm 5.1$

TABLE 5

Microcalorimetric standard ( $p^\circ = 0.1$  MPa) molar enthalpies of sublimation, at  $T = 298.15$  K, of *N*-(diethylaminothiocarbonyl)-*N'*-monoethylbenzamidine (DATMB), and *N*-(diethylaminothiocarbonyl)benzimidazole ethylester (DATBE)

Compound	Number of experiments	$T/\text{K}$	$\frac{\Delta_{cr,298\text{K}}^\circ H_m^\circ}{\text{kJ} \cdot \text{mol}^{-1}}$	$\frac{\Delta_{298.15\text{K}}^\circ H_m^\circ(\text{g})}{\text{kJ} \cdot \text{mol}^{-1}}$	$\frac{\Delta_{cr}^\circ H_m^\circ(T = 298.15\text{K})}{\text{kJ} \cdot \text{mol}^{-1}}$
DATMB	5	416.8	$185.2 \pm 1.2$	44.0	$141.2 \pm 1.2$
DATBE	5	401.3	$172.0 \pm 2.6$	36.4	$135.6 \pm 2.6$

Table 3 lists the individual values of  $\Delta_c u^\circ$  together with the mean and its standard deviation of the mean.

Table 4 lists the derived standard molar values for the energies and enthalpies of reactions  $\Delta_c U_m^\circ$ ,  $\Delta_c H_m^\circ$ , the standard molar enthalpy of formation  $\Delta_f H_m^\circ$ , of the crystalline solids, as well as the standard molar enthalpies of sublimation and the standard molar enthalpies of formation in the gaseous state. In accordance with the normal thermochemical practice, the uncertainties assigned to the standard molar enthalpies of combustion and formation are twice the overall standard deviation of the mean and include the uncertainties in calibration and in the auxiliary quantities used. To derive  $\Delta_f H_m^\circ(\text{cr})$  from  $\Delta_c H_m^\circ(\text{cr})$ , the standard molar enthalpies of formation of  $\text{H}_2\text{O}(\text{l})$ ,  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{SO}_4$  in  $115\text{H}_2\text{O}(\text{l})$ , at  $T = 298.15$  K, respectively,  $-(285.830 \pm 0.042) \text{ kJ} \cdot \text{mol}^{-1}$  [27],  $-(393.51 \pm 0.13) \text{ kJ} \cdot \text{mol}^{-1}$  [27], and  $-(887.81 \pm 0.01) \text{ kJ} \cdot \text{mol}^{-1}$  [15] were used.

Results of the measurements of the enthalpies of sublimation for *N*-(diethylaminothiocarbonyl)-*N'*-monoethylbenzamidine and *N*-(diethylaminothiocarbonyl)-benzimidazole ethylester, obtained from the Calvet microcalorimetry drop-method, are given in table 5 with uncertainties equal to twice the standard deviation of the mean.

## 5. Discussion

At present, only a limited number of thermochemical studies on compounds containing similar structures are available. Due to the complexity of the molecules, the standard molar enthalpies of formation of the investigated compounds in the gaseous state are not accessible applying group additivity methods.

Nevertheless, the enthalpy of formation in the gaseous phase, for the *N*-(diethylaminothiocarbonyl)-*N'*-monoethylbenzamidine (DATMB:  $\text{PhC}(\text{NHEt})\text{NCSNET}_2$ ) can be estimated applying data obtained from group methods, using the value of the standard molar enthalpy of formation of *N*-(diethylaminothiocarbonyl)-benzamidine (DATB:  $\text{PhC}(\text{NH}_2)\text{NCSNET}_2$ ) as an anchor. The differences between

the standard molar enthalpies of formation caused by the substituent R in the carbon atom in the structure of the compounds  $\text{PhCRNCSNET}_2$ ,  $\text{R} = -\text{NH}_2$  (DATB) and  $\text{R} = -\text{NHEt}$  (DATMB), can be estimated using the Benson's Group parameters [28] for the enthalpies of formation in the gaseous phase:  $[\text{N}-(\text{C})(\text{H})_2] = 20.08 \text{ kJ} \cdot \text{mol}^{-1}$ ,  $[\text{N}-(\text{C})_2(\text{H})] = 64.43 \text{ kJ} \cdot \text{mol}^{-1}$ ,  $[\text{C}-(\text{N})(\text{C})(\text{H})_2] = -27.61 \text{ kJ} \cdot \text{mol}^{-1}$ ,  $[\text{C}-(\text{C})(\text{H})_3] = -42.17 \text{ kJ} \cdot \text{mol}^{-1}$ . The estimated value for the  $\Delta_f H_m^\circ(\text{g})$  of the *N*-(diethylaminothiocarbonyl)-*N'*-monoethylbenzamidine (DATMB),  $99.2 \text{ kJ} \cdot \text{mol}^{-1}$ , is in good agreement with the obtained experimental result.

Applying the same strategy for an estimation of the enthalpy of formation in the gaseous phase,  $\Delta_f H_m^\circ(\text{g})$ , of *N*-(diethylaminothiocarbonyl)-*N'*-diethylbenzamidine [DATDB:  $\text{PhC}(\text{NET}_2)\text{NCSNET}_2$ ], will not work out. *N*-(diethylaminothiocarbonyl)-benzamidine [DATB:  $\text{PhC}(\text{NH}_2)\text{NCSNET}_2$ ] and *N*-(diethylaminothiocarbonyl)-*N'*-monoethylbenzamidine [DATMB:  $\text{PhC}(\text{NHEt})\text{NCSNET}_2$ ] are forming intramolecular hydrogen-sulfur-bonds in the gas phase, as indicated by the optimized geometry obtained *via* DFT calculations, which explains the intrinsic energetic difference to *N*-(diethylaminothiocarbonyl)-*N'*-diethylbenzamidine (DATDB:  $\text{PhC}(\text{NET}_2)\text{NCSNET}_2$ ) with its impossibility concerning hydrogen-bond-formation.

Due to the lack of data, the enthalpy of formation, in the gaseous phase, of the *N*-(diethylaminothiocarbonyl)-benzimidazole ethylester (DATBE:  $\text{PhC}(\text{OEt})\text{NCSNET}_2$ ) cannot be estimated following the application of a group scheme, as just described.

Table 6 presents a summary of the results, as well as the estimates derived by B3LYP calculation, anchoring all values at the standard molar enthalpy of formation of *N*-(diethylaminothiocarbonyl)-benzamidine [DATB:  $\text{PhC}(\text{NH}_2)\text{NCSNET}_2$ ], in the gaseous state [8].

The standard molar enthalpies of formation of both compounds, obtained from DFT calculations, using the enthalpies of group exchange reactions, are in good agreement with the experimental results, although the complexity of the compounds. These results show that a feasible

TABLE 6

Derived standard ( $p^\circ = 0.1$  MPa) molar enthalpies of formation in the gas phase  $\Delta_f H_m^\circ(\text{g})$ , of *N*-(diethylaminothiocarbonyl)-*N'*-monoethylbenzamidine (DATMB), and *N*-(diethylaminothiocarbonyl)benzimidazole ethylester (DATBE), at  $T = 298.15$  K

Compounds	$\Delta_f H_m^\circ(\text{g})/(\text{kJ} \cdot \text{mol}^{-1})$		
	Experimental	Group scheme	DFT/B3LYP
PhC(NHEt)NCSNET <sub>2</sub> (DATMB)	$95.5 \pm 4.6$	99.2	99.9
PhC(OEt)NCSNET <sub>2</sub> (DATBE)	$-40.6 \pm 5.1$		-37.4

estimation of the standard molar enthalpies of formation in the gaseous state can be done using group exchange reactions anchoring the calculation on experimental data, holding for similar compounds.

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