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Enthalpies of combustion of two bis(*N*,*N*-diethylthioureas)

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Abstract

The standard ($p^\circ = 0.1$ MPa) molar energies of combustion in oxygen, at $T = 298.15$ K, of two crystalline bis(*N*,*N*-diethylthioureas) $R(CONHCSNEt_2)_2$: pyridine-2,6-dicarbonyl-bis(*N*,*N*-diethylthiourea), R = pyridyl, abbreviated as (bis-py-DETU), and adipoyl-dicarbonyl-bis(*N*,*N*-diethylthiourea), $R = (CH_2)_4$, abbreviated as (bis-ad-DETU), were measured by rotating bomb calorimetry so, the standard molar enthalpies of formation of both compounds, in their crystalline phase, were derived.

Compound	$-\Delta_c U^\circ_m(\mathrm{cr})$	$-\Delta_f H^\circ_m(\mathrm{cr})$
	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$
Pyridine-2,6-dicarbonyl-bis(*N*,*N*-diethylthiourea) [bis-py-DETU]	11027.1 ± 5.2	425.2 ± 5.6
Adipoyl-dicarbonyl-bis(*N*,*N*-diethylthiourea) [bis-ad-DETU]	11124.6 ± 5.7	644.4 ± 6.1

Furthermore, the energetics of the title compounds were studied by means of density functional theory calculations at the B3LYP/ 6-311G(dp) level of theory.

Keywords: Energy of combustion; Enthalpy of formation; Pyridine-2,6-dicarbonyl-bis(*N*,*N*-diethylthiourea); Adipoyl-dicarbonyl-bis(*N*,*N*-diethylthiourea)

1. Introduction

Over the past two decades, various substituted *N*-acylthioureas have been the subject of investigations, including the thermodynamics of the complexation reactions towards metal ions in solution, thus affording conclusions on their extraction properties [1,2]. More recently, the thermochemistry of this group of compounds became the subject of interest [3].

In this work, the scope was extended to bis(*N*,*N*-diethylthioureas). By symmetric linking of two bidentate *N*-acylthioureas, quadridentate bis-*N*-acylthioureas become available.

These ligand systems are potentially bis-bidentate, with the capability of complex formation towards polyvalent metal ions, resulting in stable inner chelates with S,O-coordination. They already have been scrutinized concerning their complexation behavior, revealing the formation of oligomeric or polymeric, cyclic or chain chelates [4,5].

This work is part of an extensive study on the thermochemistry of 1,3-ligand systems with (S,O,N) ligator atoms, to contribute to the understanding of the binding process in complexation reactions towards various transition metal ions.The enthalpies of combustion of bis-py-DETU, pyridine-2,6-dicarbonyl-bis(*N*,*N*-diethylthiourea) and

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bis-ad-DETU, adipoyl-dicarbonyl-bis(*N*,*N*-diethylthiourea), as shown in figure 1, were measured, at $T = 298.15$ K, by rotating bomb calorimetry and the standard molar enthalpies of formation in crystalline state were derived.

2. Experimental

The bis(*N*,*N*-diethylthioureas) were prepared as described earlier [6]: 0.2 mol of the corresponding dichloride was added drop wise to a boiling mixture of 0.4 mol potassium thiocyanate and 250 cm^3 of dried acetone. The reaction mixture was boiled under reflux for 20 min. The precipitated potassium chloride was filtered off from the formed solution of diisothiocyanate. After adding of 0.41 mol of diethyl amine to the filtrate under simultaneously heating, the mixture was kept aside overnight. After a few hours the corresponding bis(*N*,*N*-diethylthiourea) was yielded in pale, yellow crystals.

The purities of the samples were checked by elemental analysis; the mass fraction w of C, H, N and S were as follows: for bis-py-DETU, $C_{17}H_{25}N_5O_2S_2$, found $10^2\ w(\text{C}) = 51.39$, $10^2\ w(\text{H}) = 6.35$, $10^2\ w(\text{N}) = 17.43$, $10^2\ w(\text{S}) = 16.13$, calculated $10^2\ w(\text{C}) = 51.62$, $10^2\ w(\text{H}) = 6.37$, $10^2\ w(\text{N}) = 17.71$, $10^2\ w(\text{S}) = 16.21$; for bis-ad-DETU, $C_{16}H_{30}N_4O_2S_2$, found $10^2\ w(\text{C}) = 51.21$, $10^2\ w(\text{H}) = 8.04$, $10^2\ w(\text{N}) = 15.01$, $10^2\ w(\text{S}) = 17.06$, calculated $10^2\ w(\text{C}) = 51.31$, $10^2\ w(\text{H}) = 8.07$, $10^2\ w(\text{N}) = 14.96$, $10^2\ w(\text{S}) = 17.12$.

The relative atomic masses used were those recommended by the IUPAC Commission in 2001 [7], yielding the molar masses of $395.550\ \text{g} \cdot \text{mol}^{-1}$ and $374.571\ \text{g} \cdot \text{mol}^{-1}$, respectively, for bis-py-DETU and for bis-ad-DETU.

2.1. Combustion calorimetry

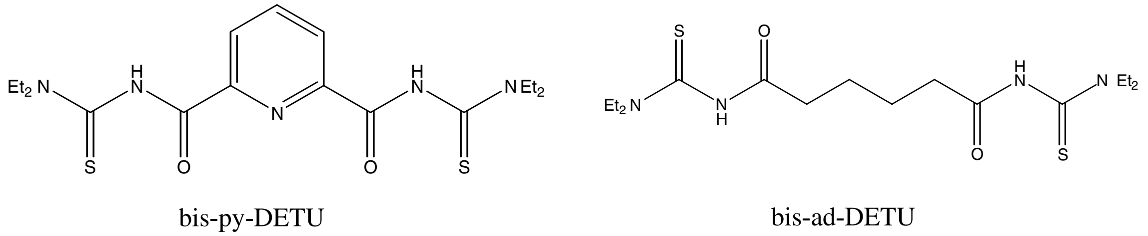
The enthalpies of combustion were measured with the rotating-bomb calorimeter formerly used at the National Physical Laboratory, Teddington, UK [8], with a platinum-lined bomb of internal volume $0.337\ \text{dm}^3$. Water was added to the calorimeter from a weighted acrylic vessel, and for each experiment a correction to the energy equivalent was made for the deviation from 4059.0 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 was automatically included in the correction for heat exchange and work of stirring by using the procedure described by Good *et al.* [9] Data acquisition and control of the calorimeter was performed using the program LABTERMO [10].

The energy equivalent of the calorimeter was determined from the combustion of benzoic acid (Bureau of Analysed Samples; Thermochemical Standard BAS-CRM 190-r), having a massic energy of combustion under bomb conditions of $-(26431.8 \pm 3.7)\ \text{J} \cdot \text{K}^{-1}$, as described previously [11]. 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 $CH_{1.686}O_{0.843}$) the massic energy of combustion is assigned to $\Delta_c u^\circ = -16240\ \text{J} \cdot \text{g}^{-1}$ [9], a value which was 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 $0.1\ \text{mol} \cdot \text{dm}^{-3}$ HNO_3(aq) from O_2, N_2, and H_2O (l) [12]. From eight calibration experiments the energy equivalent of the calorimeter, $\varepsilon(\text{calor})/(\text{J} \cdot \text{K}^{-1})$ was found to be $\{20677.1\ \pm 3.5\ (0.017\%)\}$ for an average mass of water added to the calorimeter of 4059.0 g; the quoted uncertainty is 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 $10.00\ \text{cm}^3$ of water added to the bomb. The amount of nitric acid produced was determined by ion chromatography. The densities of the two crystalline bis(*N*,*N*-diethylthioureas) were assumed to be $1.3\ \text{g} \cdot \text{cm}^{-3}$. For each compound, $(\partial u/\partial p)_T$ at $T = 298.15$ K was assumed to be $-0.2\ \text{J} \cdot \text{g}^{-1} \cdot \text{MPa}^{-1}$, a typical value for organic compounds [13]. The standard state corrections were calculated by the procedures given by Hubbard *et al.* [14] and by Good and Scott [15].

3. Computational thermochemistry details

For all involved species, full geometry optimizations with Becke's three-parameter exchange functional [16] in combination with the Lee, Yang and Parr correlation func-



bis-py-DETU bis-ad-DETU

FIGURE 1. General formula of the two bis(*N*,*N*-diethylthioureas). bis-py-DETU: Pyridine-2,6-dicarbonyl-bis(*N*,*N*-diethylthiourea); bis-ad-DETU: Adipoyl-dicarbonyl-bis(*N*,*N*-diethylthiourea).

tion as hybrid functional (B3LYP) [17] at a 6-311G(d,p)-level of theory were performed first, using the implementation of DFT in the Gaussian03 suite of programs [18]. The zero-point energies (ε_{ZPE}) are scaled to 0.9804 [19]. Harmonic vibrational frequencies were calculated at the same level of theory, applying a scaling factor 0.9613 for the correction of anharmonicity [19].

4. Results

Table 1 lists typical combustion results for each compound in which $\Delta m(\mathrm{H_2O})$ is the deviation of the mass added to the calorimeter from 4059.0 g, the mass assigned to ε(calor), and ΔU_Σ is the correction to the standard state. The remaining quantities are as previously described [14]. Details of all the Combustion Calorimetry experiments are given in the Supporting Information, in Tables S1 and S2.

The internal energy for the isothermal bomb process, ΔU(IBP), was calculated according to the following equation:

$$\Delta U(\mathrm{IBP}) = -\{\varepsilon(\mathrm{calor}) + c_\mathrm{p}(\mathrm{H_2O,l})\Delta m(\mathrm{H_2O})\}\Delta T_\mathrm{ad} + (T_\mathrm{i} - 298.15)\varepsilon_\mathrm{i} + (298.15 - T_\mathrm{i} - \Delta T_\mathrm{ad})\varepsilon_\mathrm{f} + \Delta U(\mathrm{ign}), \tag{1}$$

where ΔT_ad is the calorimeter temperature change corrected for the heat exchange and the work of stirring.

TABLE 1
Typical combustion experimental results of pyridine-2,6-dicarbonyl-bis(*N*,*N*-diethylthiourea) (bis-py-DETU) and adipoyl-dicarbonyl-bis(*N*,*N*-diethylthiourea) (bis-ad-DETU), at $T = 298.15$ K

	bis-py-DETU	bis-ad-DETU
m(cpd.)/g	0.72465	0.75689
m'(fuse)/g	0.00383	0.00555
T_i/K	297.1680	297.2154
T_f/K	298.1845	298.3362
ΔT_ad/K	0.98134	1.09258
ε_i(cont.)/(J.K^{-1})	53.3	53.4
ε_f(cont.)/(J.K^{-1})	53.0	53.4
$\Delta m(\mathrm{H_2O})$/g	−2.1	−1.0
$-\Delta U(\mathrm{IBP})^a$/J	20333.8	22644.0
$\Delta U(\mathrm{HNO_3})$/J	46.9	47.6
ΔU(ignition)/J	1.2	1.2
ΔU_Σ/J	23.1	21.4
$m' \cdot \Delta_\mathrm{c}u^\circ$ (fuse)/J	62.2	90.1
$-\Delta_\mathrm{c}u^\circ(\mathrm{cpd.})/\mathrm{J \cdot g^{-1}}$	27877.7	29707.0

m(cpd.) is the mass of compound burnt in each experiment; m'(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; ΔT_ad is the corrected temperature rise; ε_i(cont.) is the energy equivalent of the contents in the initial state; ε_f(cont.) is the energy equivalent of the contents in the final state; $\Delta m(\mathrm{H_2O})$ is the deviation of mass of water added to the calorimeter from 4059.0 g; ΔU(IBP) is the energy change for the isothermal combustion reaction under actual bomb conditions; $\Delta U(\mathrm{HNO_3})$ is the energy correction for the nitric acid formation; ΔU(ignition) is the electric energy for the ignition; ΔU_Σ is the standard state correction; $\Delta_\mathrm{c}u^\circ$ (fuse) is the massic energy of combustion of the fuse (cotton); $\Delta_\mathrm{c}u^\circ$ is the standard massic energy of combustion.

[a] ΔU(IBP) includes ΔU(ignition).

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 $\Delta_\mathrm{c}u^\circ$ refer to the reactions represented by equations (2) and (3), for bis-py-DETU and bis-ad-DETU, respectively:

bis-py-DETU:

$$\mathrm{C_{17}H_{25}O_2N_5S_2\ (cr) + 25.25\ O_2\ (g) + 219.5\ H_2O\ (l) \rightarrow 17\ CO_2\ (g) + 2.5\ N_2\ (g) + 2[H_2SO_4 \cdot 115H_2O]\ (l)} \tag{2}$$

bis-ad-DETU:

$$\mathrm{C_{16}H_{30}O_2N_4S_2\ (cr) + 25.5\ O_2\ (g) + 217\ H_2O\ (l) \rightarrow 16\ CO_2\ (g) + 2\ N_2\ (g) + 2[H_2SO_4 \cdot 115H_2O]\ (l).} \tag{3}$$

Table 2 lists, for each compound, the individual values of $\Delta_\mathrm{c}u^\circ$, together with the mean and the standard deviation of the mean.

Table 3 lists the derived standard molar values for the energies and enthalpies of combustion, $\Delta_\mathrm{c}U^\circ_\mathrm{m}$, $\Delta_\mathrm{c}H^\circ_\mathrm{m}$, respectively, as well as the standard molar enthalpies of formation, $\Delta_\mathrm{f}H^\circ_\mathrm{m}$, of the crystalline solids, at $T = 298.15$ K. In accordance with the normal thermochemical practice, the uncertainties assigned to the standard molar enthalpies of combustion and formation are twice the overall standard

TABLE 2
Individual values of the standard ($p^\circ = 0.1$ MPa) massic energy of combustion, $\Delta_\mathrm{c}u^\circ$,of Pyridine-2,6-dicarbonyl-bis(*N*,*N*-diethylthiourea) (bis-py-DETU) and of Adipoyl-dicarbonyl-bis(*N*,*N*-diethylthiourea) (bis-ad-DETU), at $T = 298.15$ K

bis-py-DETU	bis-ad-DETU
$-\Delta_\mathrm{c}u^\circ/(\mathrm{J \cdot g^{-1}})$	
27877.7	29707.0
27876.9	29695.7
27870.3	29712.8
27881.8	29699.1
27882.9	29706.3
	29694.7
	29681.5
$-\langle\Delta_\mathrm{c}u^\circ\rangle/(\mathrm{J \cdot g^{-1}})^a$	
27877.9 ± 2.2	29699.6 ± 3.9

The mean values are represented by $\langle\Delta_\mathrm{c}u^\circ\rangle$.

[a] Mean value; given uncertainty as the standard deviation of the mean.

TABLE 3
Derived standard ($p^\circ = 0.1$ MPa) molar energies of combustion, $\Delta_\mathrm{c}H^\circ_\mathrm{m}$, standard molar enthalpies of combustion, $\Delta_\mathrm{c}H^\circ_\mathrm{m}$, standard molar enthalpies of formation, (cr), for Pyridine-2,6-dicarbonyl-bis(*N*,*N*-diethylthiourea) (bis-py-DETU) and Adipoyl-dicarbonyl-bis(*N*,*N*-diethylthiourea) (bis-ad-DETU), at $T = 298.15$ K

Compound	$-\Delta_\mathrm{c}H^\circ_\mathrm{m}(\mathrm{cr})/(\mathrm{kJ \cdot mol^{-1}})$	$-\Delta_\mathrm{c}H^\circ_\mathrm{m}(\mathrm{cr})/(\mathrm{kJ \cdot mol^{-1}})$	$-\Delta_\mathrm{f}H^\circ_\mathrm{m}(\mathrm{cr})/(\mathrm{kJ \cdot mol^{-1}})$
Bis-py-DETU	11027.1 ± 5.2	11041.3 ± 5.2	425.2 ± 5.6
Bis-ad-DETU	11124.6 ± 5.7	11143.2 ± 5.7	644.4 ± 6.1

deviation of the mean and include the uncertainties in calibration and in the auxiliary quantities used. To derive $\Delta_f H^\circ_m$(cr) from $\Delta_c H^\circ_m$(cr), the standard molar enthalpies of formation of H_2O(l), CO_2(g) and H_2SO_4 in 115 H_2O(l), at $T = 298.15$ K, respectively, $-(285.830 \pm 0.042)$ kJ · mol^{-1} [20], $-(393.51 \pm 0.13)$ kJ · mol^{-1} [20], and $-(887.81 \pm 0.4)$ kJ · mol^{-1} [12] were used.

5. Discussion

There are no previously determined values for the standard molar enthalpies of formation of these compounds as, at present, only a limited number of thermochemical studies on compounds containing similar structures are available.

In both cases, it was not possible to measure the standard molar enthalpies of sublimation due to thermal decomposition reactions of the compounds occurring at comparatively low temperatures. Therefore, we cannot derive the respective standard molar enthalpies of formation in the gas phase, $\Delta_f H^\circ_m$ (g). However, the comparison with substances with the same structural motifs allows for estimations of the standard molar enthalpies of sublimation in question: assuming that the standard molar enthalpies of sublimation of bis-py-DETU [pyridine-2,6-dicarbonyl-bis(*N*,*N*-diethylthiourea)] and bis-ad-DETU [adipoyl-dicarbonyl-bis(*N*,*N*-diethylthiourea)] are nearly equal $\{\Delta(\Delta^g_{cr} H^\circ_m) = (0 \pm 10)\ \mathrm{kJ \cdot mol^{-1}}\}$, the reaction enthalpy of the following empirical group exchange reaction can be derived:

$$\begin{aligned}&\text{bis-py-DETU (g)} + n\text{-butane (g)} \rightarrow \\ &\quad \text{bis-ad-DETU (g)} + \text{pyridine (g)}, \end{aligned} \tag{4}$$

with

$$\begin{aligned}\Delta_r H^\circ_m\,(4) = {}& \Delta_f H^\circ_m\,(\text{bis-ad-DETU,cr}) - \\ & \Delta_f H^\circ_m\,(\text{bis-py-DETU,cr}) + \Delta_f H^\circ_m\,(\text{pyridine,g}) - \\ & \Delta_f H^\circ_m\,(n\text{-butane,g}) + \Delta(\Delta^g_{cr} H^\circ_m).\end{aligned} \tag{5}$$

Using $\Delta_f H^\circ_m$ (pyridine, g) = (140.6 ± 1.5) kJ · mol^{-1} [21] and $\Delta_f H^\circ_m$ (n-butane, g) = $-(125.6 \pm 0.67)$ kJ · mol^{-1} [22], we can derive $\Delta_r H^\circ_m$ (4) = (47 ± 12) kJ · mol^{-1}.

This can be compared with another empirical group exchange reaction, where the functional groups of the title compounds have merely been replaced by acetyl groups:

$$\begin{aligned}&\text{2, 6-Diacetylpyridine(g)} + n\text{-butane(g)} \rightarrow \\ &\quad \text{1, 4-Diacetylbutane(g)} + \text{pyridine(g)},\end{aligned} \tag{6}$$

with

$$\begin{aligned}\Delta_r H^\circ_m\,(6) = {}& \Delta_f H^\circ_m\,(\text{1,4-diacetylbutane, g}) - \\ & \Delta_f H^\circ_m\,(\text{2,6-diacetylpyridine, g}) + \\ & \Delta_f H^\circ_m\,(\text{pyridine, g}) - \Delta_f H^\circ_m\,(n\text{-butane, g}).\end{aligned} \tag{7}$$

Unfortunately, experimental values for the standard molar enthalpies of formation in the gas phase, $\Delta_f H^\circ_m$(g), for both compounds, are not known. Applying bond-energy schemes with the previously established [23] parameters **C**–(H)$_3$(C) = −42.7 kJ · mol^{-1}, **C**–(H)$_2$(C)$_2$ = −21 kJ · mol^{-1}, **C**(H)$_2$(CO)(C) = −22 kJ · mol^{-1}, **CO**(C)$_2$ =−131 kJ · mol^{-1}, **C**$_B$(CO) = 15 kJ · mol^{-1}, **C**$_B$(H) = 14 kJ · mol^{-1}, **CO**(C)(C$_B$) = −129 kJ · mol^{-1} and **N**$_{\mathbf{pyr}}$–(C$_B$) = 69.9 kJ · mol^{-1}, the following enthalpies of formation were estimated: for: 4-diacetylbutane, $\Delta_f H^\circ_m(C_8H_{14}O_2, g)$ = 2 · **C**–(H)$_3$(C) + 2 · **C**–(H)$_2$(C)$_2$ + 2 · **C**(H)$_2$(CO)(C) + 2 · **CO**(C)$_2$ = −433.4 kJ · mol^{-1}, and for 2,6-diacetylpyridine, $\Delta_f H^\circ_m(C_9H_9NO_2, g)$ = 2 · **C**–(H)$_3$(C) + 2 · **C$_B$**(CO) + 3**C$_B$**–(H)+ 2 · **CO**(C)(C$_B$) +**N**$_{\mathbf{pyr}}$–(C$_B$) = −201.5 kJ · mol^{-1}. Using these values, the enthalpy of the exchange reaction (6) is calculated as $\Delta_r H^\circ_m(6)$ = +34.3 kJ · mol^{-1}.

The *ab initio* B3LYP calculation at 6-311G(d,p) level of the same reaction gives $\Delta_r H^\circ_m$ (6) = +39.9 kJ · mol^{-1}, which is in good agreement with the group scheme estimate. Turning back now to reaction (4) and calculating the enthalpy of the empirical group exchange reaction via DFT/B3LYP at the same level of theory, we obtain $\Delta_r H^\circ_m$ (4) = +54.2 kJ · mol^{-1} which is also in agreement with the experimental value $\Delta_r H^\circ_m$ (4) = +(47 ± 12) kJ · mol^{-1}. Table 4 shows the total energies of the reactants of both the empirical group exchange reactions, with the assigned energy corrections.

The results of the DFT/B3LYP calculations indicate that, for the applied level of theory, the enthalpy of the empirical group exchange reaction can be calculated rather precise. Furthermore, this allows for the standard molar enthalpies of formation in gas phase, $\Delta_f H^\circ_m$(g), to be estimated with a sufficient accuracy – provided that, at least, the standard molar enthalpy of formation in gas phase of one of the reactants of the chosen empirical group exchange reaction is known.

TABLE 4
Total energies in kJ · mol^{-1} of the reactants of the empirical group exchange reactions (4) and (6)

Energy	bis-py-DETU	bis-ad-DETU	Pyridine	n-Butane	2,6-Diacetylpyridine	1,4-Diacetylbutane
ε_0	−4946029.47	−4710097.29	−652034.62	−416154.74	−1453809.22	−1217887.704
$\varepsilon_0 + \varepsilon_{ZPE}$ (scaled to 0.9804)	−4944951.70	−4708905.29	−651806.93	−415816.31	−1453391.69	−1217358.482
$\varepsilon_0 + \varepsilon_{ZPE}$ (scaled to 0.9804) + H_{corr} (scaled to 0.9613)	−4944873.41	−4708824.58	−651792.86	−415798.30	−1453358.26	−1217323.799

Full geometry optimizations with the B3LYP functional at a 6-311G(d,p)-level of theory were performed first, followed by frequency calculations at the same level of theory. bis-py-DETU: pyridine-2,6-dicarbonyl-bis(*N*,*N*-diethylthiourea). bis-ad-DETU: Adipoyl-dicarbonyl-bis(*N*,*N*-diethylthiourea). Assigned energy corrections to the total energy (kJ · mol^{-1}): ε_0 – total electronic energy, ε_{ZPE} – zero-point energy, H_{corr} – thermal enthalpy.

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Appendix A. Supplementary data

Tables S1 and S2 listing the details of all the Combustion Calorimetry experiments, at $T = 298.15$ K, for pyridine-2,6-dicarbonyl-bis(*N*,*N*-diethylthiourea) and adipoyl-dicarbonyl-bis(*N*,*N*-diethylthiourea). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jct.2006.07.007.

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