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

Manuel A.V. Ribeiro da Silva [a,*], Luis M.N.B.F. Santos [a], Bernd Schröder [a],
Lothar Beyer [b], Frank Dietze [b]

[a] *Centro de Investigação em Química, Departamento de Química, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, 687, P-4169-007 Porto, Portugal*
[b] *Institut für Anorganische Chemie, Universität Leipzig, Johannisallee 29, D-04103 Leipzig, Germany*

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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	$-\Delta_c U^\circ_m(\text{cr})$	$-\Delta_f H^\circ_m(\text{cr})$
	$\text{kJ} \cdot \text{mol}^{-1}$	$\text{kJ} \cdot \text{mol}^{-1}$
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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[*] Corresponding author. Tel.:+351 22 6082 821; fax: +351 22 6082 822.
E-mail address: risilva@fc.up.pt (M.A.V. Ribeiro da Silva).

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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

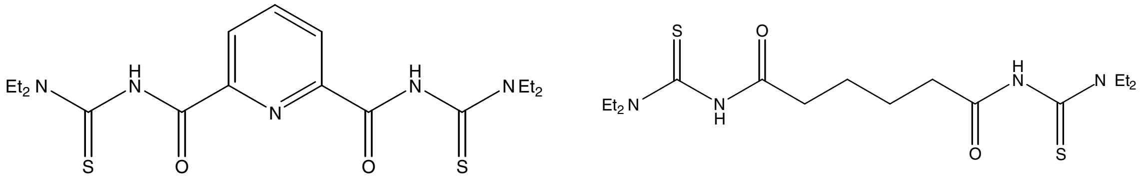
The enthalpies of combustion were measured with the rotating-bomb calorimeter formerly used at the National Physical Laboratory, Teddington, UK [8], with a platinum-lined bomb of internal volume $0.337\ \text{dm}^3$. Water was added to the calorimeter from a weighted acrylic vessel, and for each experiment 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).