



Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: [www.elsevier.com/locate/jct](http://www.elsevier.com/locate/jct)

# Thermochemistry of 1,3-diethylbarbituric and 1,3-diethyl-2-thiobarbituric acids: Experimental and computational study



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## ARTICLE INFO

### Article history:

Received 28 April 2014

Received in revised form 29 May 2014

Accepted 2 June 2014

Available online 11 June 2014

### Keywords:

1,3-Diethylbarbituric acid

1,3-Diethyl-2-thiobarbituric acid

Enthalpy of formation

Enthalpy of combustion

Enthalpy of sublimation

Enthalpy of vaporization

Vapor pressure

G3 and G4 calculations

## ABSTRACT

This paper reports an experimental and computational thermochemical study on two barbituric acid derivatives, viz. 1,3-diethylbarbituric acid and 1,3-diethyl-2-thiobarbituric acid. Values of standard molar enthalpies of formation in the gas phase at  $T = 298.15$  K have been derived from experiment. Energies of combustion were measured by the static bomb combustion calorimetry in the case of 1,3-diethylbarbituric acid, and the rotating-bomb combustion calorimetry in the case of 1,3-diethyl-2-thiobarbituric acid. From the combustion energies, standard molar enthalpies of formation in the crystalline state at  $T = 298.15$  K were calculated. The enthalpy of vaporization of 1,3-diethylbarbituric acid and enthalpy of sublimation of 1,3-diethyl-2-thiobarbituric acid were determined using the transpiration method. Combining calorimetric and transpiration results, values of  $-(611.9 \pm 2.0)$  kJ·mol<sup>-1</sup> and  $-(343.8 \pm 2.2)$  kJ·mol<sup>-1</sup> for the gas-phase enthalpies of formation at  $T = 298.15$  K of 1,3-diethylbarbituric and 1,3-diethyl-2-thiobarbituric acids, respectively, were derived. Theoretical calculations at the G3 and G4 levels were performed, and a study of the molecular structure of the compounds has been carried out. Calculated enthalpies of formation were in very good agreement with the experimental values.

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## 1. Introduction

Over the past years, we have been involved in the study of the thermochemistry of barbituric acid (2,4,6(1*H*,3*H*,5*H*)-pyrimidine-trione) and its derivatives, with the aim of understanding the structural effects on their thermodynamic stabilities as reflected in the gas-phase enthalpy of formation. We have published thermochemical studies of the parent compound barbituric acid [1], its 5,5-dimethyl [2], 1,3-dimethyl [3], 5,5-diethyl (barbital) [4,5], 1,3,5-trimethyl, 1,5,5-trimethyl, and 1,3,5,5-tetramethyl [6] derivatives, and also of a sulfur-containing barbituric acid, 2-thiobarbituric acid [7]. We have also reported thermophysical studies of some methyl and ethyl derivatives of barbituric acid [8], and of 2-thiobarbituric acid [9]. Finishing these series of studies, in the present work we have carried out an experimental and computational study on the energy-structure relationships for two ethyl derivatives: 1,3-diethylbarbituric acid (1,3-diethyl-2,4,6(1*H*,3*H*,5*H*)-pyrimidinetrione) [CAS 32479-73-5], and 1,3-diethyl-2-thiobarbituric acid

(1,3-diethyl-2-thioxodihydro-4,6(1*H*,5*H*)-pyrimidinedione) [CAS 5217-47-0], whose structures are presented in figure 1.

## 2. Experimental

### 2.1. Materials and purity control

The preparation and purification of 1,3-diethylbarbituric acid was described in detail in our previous publication [8]. It was re-crystallized from the mixture of chloroform and heptane with a volume ratio of 1.4:1. The 1,3-diethyl-2-thiobarbituric acid was commercially available from Aldrich. This sample was purified by the fractional sublimation. Provenance, purification, and analysis details of the samples under study are given in table 1.

### 2.2. Static bomb combustion calorimetry

The energy of combustion of 1,3-diethylbarbituric acid was measured in the isoperibol calorimeter equipped with the static bomb. The detailed procedure has been described previously [11]. The solid sample was pressed into a pellet and weighed using

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