Thermophysical Study of 2-Thiobarbituric Acids by Differential Scanning Calorimetry

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S *Supporting Information*

ABSTRACT: The present study reports a differential scanning calorimetry (DSC) study of 2-thiobarbituric acid [CAS Registry No. 504-17-6] and its derivative 1,3-diethyl-2-thiobarbituric acid [CAS Registry No. 5217-47-0] in the temperature interval from $T = 268$ K to their respective melting temperatures. Temperatures, enthalpies, and entropies of fusion of both compounds are reported. 2-Thiobarbituric acid exhibits solid—solid phase transitions in the temperature interval studied. The polymorphic form of commercially available 2-thiobarbituric acid was identified by powder X-ray diffraction comparisons with the literature, and the heat capacity was measured from $T = (268 \text{ to } 430)$ K, temperatures below the first observable phase transition. The heat capacity of 1,3-diethyl-2-thiobarbituric acid was measured from $T = (268 \text{ to } 365)$ K. Commercially available 1,3-diethyl-2-thiobarbituric acid was likewise characterized by its X-ray powder diffraction pattern. Total phase change entropies and heat capacities of the two materials were also estimated by group additivity.
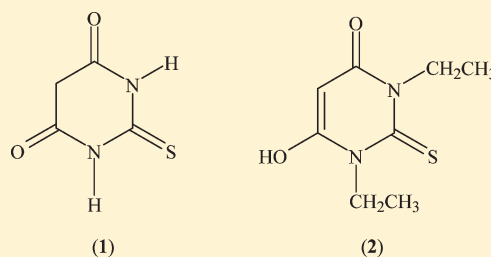
INTRODUCTION

Despite the importance and applications of barbituric acid derivatives, thermochemical and thermophysical data existing in the literature are scarce,[1,2] and sometimes there are important discrepancies among the existing values. Some of these discrepancies are probably due to the multiple polymorphic forms that some of these derivatives exhibit.[3,4]

The knowledge of heat capacity as a function of temperature is essential for the calculation of thermodynamic properties such as ΔH, ΔS, and ΔG at different temperatures, and this property plays an important role in identifying and understanding modifications occurring in the solid state of crystals and liquid crystals. Heat capacities at $T = 298.15$ K have proven quite useful in adjusting vaporization, sublimation, and fusion enthalpies with temperature. Equations for doing this have recently been summarized by Acree and Chickos.[5]

There are several compilations of critically evaluated calorimetrically measured heat capacities of organic molecules in the literature,[6–12] but new data on heat capacity for important families of compounds are still needed.[11] In this regard during the past few years, we have been involved in the experimental determination of enthalpies of fusion, heat capacities, and the study of polymorphism of pure organic compounds.

There has been an effort to develop reliable and accurate group contribution schemes to improve the estimation and compensate for the scarcity of this data. The simplest schemes are based on first-order additivity and only consider the constituent groups of the molecule.[13,14] Other methods use a second-order additivity scheme that takes into account nearest-neighbor interactions in the definition of the structural units of molecules.[15–17] These schemes normally neglect all next-to-nearest neighbor interactions because of the limited accuracy of the available experimental heat capacity data and the additional complexity necessary for their application. Although current improvements in instrumentation and protocol allow the experimental determination of heat capacities by DSC within an error of 0.15 %,[18] the actual experimental uncertainty of the measured heat capacity is larger due to the presence of impurities in the samples under investigation. Special care must be taken to remove or reduce the water content, especially for liquid samples, since the heat capacity of water departs considerably from that of the majority of organic compounds. Estimations of heat capacity of solids are more problematic than their liquid counterparts. This is due in part to the lack of data but also due to the anisotropic nature of the solid state. Phase transitions in solids can affect their heat capacities near these transitions. Solids that form liquid crystals, for example, seem to have larger heat capacities in certain temperature regions, and phase change entropies appear attenuated in comparison to systems that melt directly to isotropic liquids.[19] Group values for estimating the heat capacity of
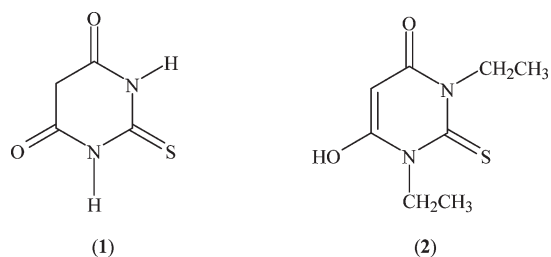
Figure 1. Some molecular structures of 2-thiobarbituric acid (**1**) and 1,3-diethyl-2-thiobarbituric acid (**2**) in the solid state.

Figure 2. Tautomeric form of commercial 2-thiobarbituric acid (**3**) and the keto tautomer of 1,3-diethyl-2-thiobarbituric acid.

crystalline solids have been reported, but the estimations in many cases have been hampered by the lack of sufficient data.

We are presently involved in a systematic thermochemical and thermophysical study of barbituric acid derivatives. We have recently published thermochemical studies of barbituric acid[20] and its 5,5-dimethyl,[21] 5,5-diethyl (barbital),[22] and 1,3-dimethyl[23] derivatives. We have also reported thermophysical studies of some methyl and ethyl barbituric acid derivatives.[24]

The present work reports the temperature, enthalpy, and entropy of fusion and heat capacities of two thiobarbituric acids measured by differential scanning calorimetry (DSC). The target compounds (see Figure 1) are 2-thiobarbituric acid (**1**) and 1,3-diethyl-2-thiobarbituric acid (**2**). An objective of this work was to expand the database of available experimental heat capacities of barbituric acid derivatives and to provide reliable data to adjust and refine group contribution schemes for the estimation of this property for compounds that have not yet been investigated.

2-Thiobarbituric acid has been previously investigated by single crystal X-ray, NMR, Raman, and X-ray powder diffraction studies and by DSC.[4] The compound is known to exist in various tautomeric polymorphic forms, all of which are converted to the structure shown in Figure 1 upon heating. The material decomposes upon melting.

The crystal structure of 1,3-diethyl-2-thiobarbituric acid determined by both X-ray crystallography and neutron diffraction shows that the molecule exists in the enol form as shown in Figure 1.[25,26] It is not known in this case whether this material is also converted to the diketo form upon heating. In this case no solid—solid phase transitions were detected over the temperature range studied.

■ EXPERIMENTAL PROCEDURES

Materials. 2-Thiobarbituric acid (**1**) [CAS Registry No. 504-17-6] (≥ 98 %) and 1,3-diethyl-2-thiobarbituric acid (**2**) [CAS Registry No. 5217-47-0] (99 %) were commercially available from Aldrich, and no further purification was necessary.

Purity Control. Both samples were carefully dried under vacuum. The determination of purity was assessed by high-performance liquid chromatography (HPLC) and DSC, using the fractional fusion technique.[27] The mole fraction of impurities in the compounds studied was less than 0.0002.

The standards used for DSC calibration were hexafluorobenzene, 99.9 % purity, supplied by Aldrich; benzoic acid, National Institute of Standards and Technology (NIST) standard reference sample 39j, and high-purity indium (mass fraction > 0.99999) and tin (mass fraction > 0.99999) supplied by Perkin-Elmer.
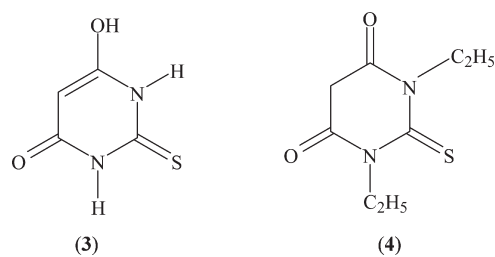
Apparatus and Procedure. The behavior of the samples as a function of temperature was studied by DSC. A Perkin-Elmer Pyris 1 instrument equipped with an intracooler unit was used to monitor purity, to study the fusion process and the possible existence of phase transitions in the solid samples, and to determine heat capacities as a function of temperature. The apparatus was previously calibrated in temperature and energy with reference materials. The temperature and power scales were calibrated[28−30] at heating rates of (0.04 and 0.17) $K \cdot s^{-1}$. The temperature scales were calibrated by the melting temperature of the high-purity reference materials, hexafluorobenzene, tin, and indium.[31] The power scales were calibrated with high-purity indium.[32]

Thermograms of samples hermetically sealed in aluminum pans were recorded in a nitrogen atmosphere. All of the pans with the samples were weighed on a Mettler AT21 microbalance with a detection limit of $1 \cdot 10^{-6}$ g before and after the experiments to confirm that no product had volatilized. The experiments where any mass loss was observed were rejected.

After calibration, several runs with high-purity benzoic acid and indium were performed under the same conditions as the experimental determinations. The accuracies associated with measurements of temperature and enthalpy of fusion were calculated as the percentage deviation of the experimental data with respect to the values given in the literature;[31] in all cases the deviations were lower than 0.2 and 2.0 % for temperature and enthalpy determinations, respectively.[32]

For determination of purity, temperature, and enthalpy of fusion, a heating rate of 0.04 $K \cdot s^{-1}$ was used, and five to eight samples weighing (1 to 2) mg were recorded. A fresh sample was used for each run. Different scans at heating rates of (0.04 and 0.17) $K \cdot s^{-1}$ were performed to determine the possible existence of phase transitions in the samples over the temperature range from $T = 268$ K to their melting temperature.

Heat capacities were determined by the "scanning method" following the experimental methodology previously described[33−35] with synthetic sapphire (α-aluminum oxide) as a reference material.[31,33−35] DSC is a commonly accepted method for the quantitative determination of heat capacities, and it has been proven as a suitable technique for obtaining reliable and accurate values.[36,37] As a check of the experimental method, heat capacity experiments were performed with benzoic acid in the temperature interval $T = (268$ to $360)$ K.[17] The relative percentage error of our measurements in comparison with those reported in the literature was less than 2 %.[32]

The mass of sapphire used in each run was 0.030345 g. For heat capacity determinations, three to six fresh samples weighing (10 to 25) mg were scanned for each solid compound. 2-Thiobarbituric acid was measured over the temperature range

Table 1. Group Values (Γ) Used to Estimate Total Phase Change Entropies and Heat Capacities

components	group (Γ)	$\Gamma(\Delta_{\text{tpce}}S(T_{\text{fus}}))^a$ $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$\Gamma(C_{p,\text{m}}(\text{cr}))^a$ $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
primary sp^3 carbon	CH$_3$−	17.6	36.6
secondary sp^3 carbon	−CH$_2$−	7.1	26.9
cyclic secondary sp^3 carbon	−CH$_2$−		24.6
cyclic sec amide	−C(=O)NH−	2.7	46.4
N-substituted cyclic tertiary amide	−C(=O)NR−	−21.7	45.3
N-substituted cyclic monothioimide^b	−C(=S)N(R)C(=O)−	[−13.6]	[49.4]^c
cyclic monothioimide^b	−C(=S)N(H)C(=O)−	[2.8]	[74.1]

^{a} Values in brackets are considered tentative assignments; group values for $\Gamma(\Delta_{\text{tpce}}S(T_{\text{fus}}))$ from ref 39; $\Gamma(C_{p,\text{m}}(\text{cr}))$ values from ref 13 unless noted otherwise. ^{b} The group value for the corresponding oxo compound was used as a substitute for this group for both $\Delta_{\text{tpce}}S(T_{\text{fus}})$ and $C_{p,\text{m}}(\text{cr})$; see text. ^{c} The value for the corresponding oxo group from ref 24.

$T = (268 \text{ to } 430)$ K and 1,3-diethyl-2-thiobarbituric acid from $T = (268 \text{ to } T_{\text{fus}})$ K, both at 0.17 K·s^{-1} as is usual in these measurements. The complete temperature range for determination of heat capacity was divided in intervals of approximately 40 K, overlapping by 5 K from one interval to another.

The molecular weights used to convert the specific heat capacities measured to their molar values were calculated from the atomic weights recommended by the International Union of Pure and Applied Chemistry (IUPAC) in 2009.[38]

X-ray Diffraction Studies. Powder X-ray diffraction analysis (PXRD hereinafter) was used to identify the polymorphic forms of the commercial samples. The powder patterns for both compounds were collected on a PANalytical XPertPRO MPD powder diffractometer (Cu Kα) at $T = 298.15$ K. The powder patterns of both commercial samples of 2-thiobarbituric acid (**1**) and 1,3-diethyl-2-thiobarbituric acid (**2**) are provided in the Supporting Information. On the basis of the comparison with previous work,[4] the tautomeric form of the commercial sample of 2-thiobarbituric acid is given as **3**, shown in Figure 2. This converts to **1** at about $T = 463$ K. The powder pattern of 1,3-diethyl-2-thiobarbituric acid is included for identification purposes should other polymorphs be identified for this material.

Estimations of Total Phase Change Entropies and Heat Capacity. Total phase change entropies were calculated according to the protocol described previously.[39] Table 1 lists group values used together with the ring equation developed, eq 1, to estimate $\Delta_{\text{tpce}}S(T_{\text{fus}})_{\text{ring}}$.

$$\Delta_{\text{tpce}}S(T_{\text{fus}})_{\text{ring}} = 33.4 + 3.7(N - 3) \tag{1}$$

The estimation of a nonaromatic monocyclic heterocycle begins by first estimating the parent hydrocarbon of ring size N, obtained by substituting carbon for all of the ring heteroatoms using eq 1. Estimations of the heterocyclic ring are then completed by identifying the appropriate groups that modify the structure and adding their contributions. The groups are identified in columns 1 and 2 of Table 1, and their contributions are listed in column 3 of the table. Both barbituric acid derivatives of this study were modeled in their keto tautomeric forms (**1** and **4**) as derivatives of cyclohexane (cyclohexane 44.5 J·mol^{-1}·K^{-1}). Modifications to the cyclohexane structure for 2-thiobarbitutic acid include the introduction of a cyclic secondary amide (−(C=O)NH−; 2.7 J·mol^{-1}·K^{-1}) and cyclic monothioimide (−(C=S)NH (C=O)−; 2.8 J·mol^{-1}·K^{-1}) to the ring. The total phase change entropy for 2-thiobarbituric acid is estimated as the sum, 50 J·mol^{-1}·K^{-1}. Since a group value for the latter is not available,

the group value for a cyclic imide was used as a substitute thereby completing the estimation of $\Delta_{\text{tpce}}S(T_{\text{fus}})$ for this compound. Similarly for 1,3-diethyl-2-thiobarbituric acid, due to the lack of sufficient group values, this compound was also modeled as its diketo tautomer **4**. The recently assigned N-substituted cyclic imide group (−C(=O)N(R)C(=O)−)[24] was used as a substitute for an N-substituted cyclic monothioimide group (−(C=S)NR(C=O)−). The addition of the contribution of an N-cyclic tertiary amide completes this estimation. The estimations for both 2-thiobarbituric acid and 1,3-diethyl-2-thiobarbituric acid are included below in Table 3.

The estimation of heat capacity follows a more traditional group additivity protocol. The groups in each molecule are identified and their contributions totalled. The group values for estimating $C_{p,\text{m}}(\text{cr})$ of the compounds of this study are listed in column 4 of Table 1. Both compounds were also estimated as their keto tautomers **1** and **4**. 2-Thiobarbituric acid was modeled as containing a cyclic secondary amide, a cyclic monothioimide and a cyclic secondary sp^3 carbon. 1,3-Diethyl-2-thiobarbituric acid was modeled as containing two ethyl groups, an N-substituted cyclic tertiary amide, an N-substituted cyclic monothioimide and a cyclic secondary sp^3 carbon. These estimations are summarized in Table 6. The group value used for a cyclic tertiary amide represents a new updated value.[24]

◼ RESULTS AND DISCUSSION

The behavior of 2-thiobarbituric acid and 1,3-diethyl-2-thiobarbituric acids in the temperature interval from $T = 373$ K to their respective melting temperature is shown in Figure 3. No other changes for 2-thiobarbituric acid were detected in the temperature interval $T = 263$ K to $T = 373$ K. From six experiments with fresh samples the values obtained for the temperatures and enthalpies of the transitions found are given in Table 2.

Five interconverting polymorphs of the keto form of 2-thiobarbituric acid have been identified and characterized.[4] The commercial form is reported to be enolic at oxygen, **3**, but is thermally converted to one of the keto polymorphs at $T = 463$ K. At $T > 498$ K, the conversion to the same keto polymorph is complete.[4]

No solid−solid phase transitions were observed over the temperature interval from $T = 268$ K to its melting temperature for 1,3-diethyl-2-thiobarbituric acid. Experimental temperatures (taken as the onset temperatures and not corrected for impurities), enthalpies, and entropies of fusion of the compounds measured are given in Table 3. The uncertainties were taken as

(a)

(b)

(c)
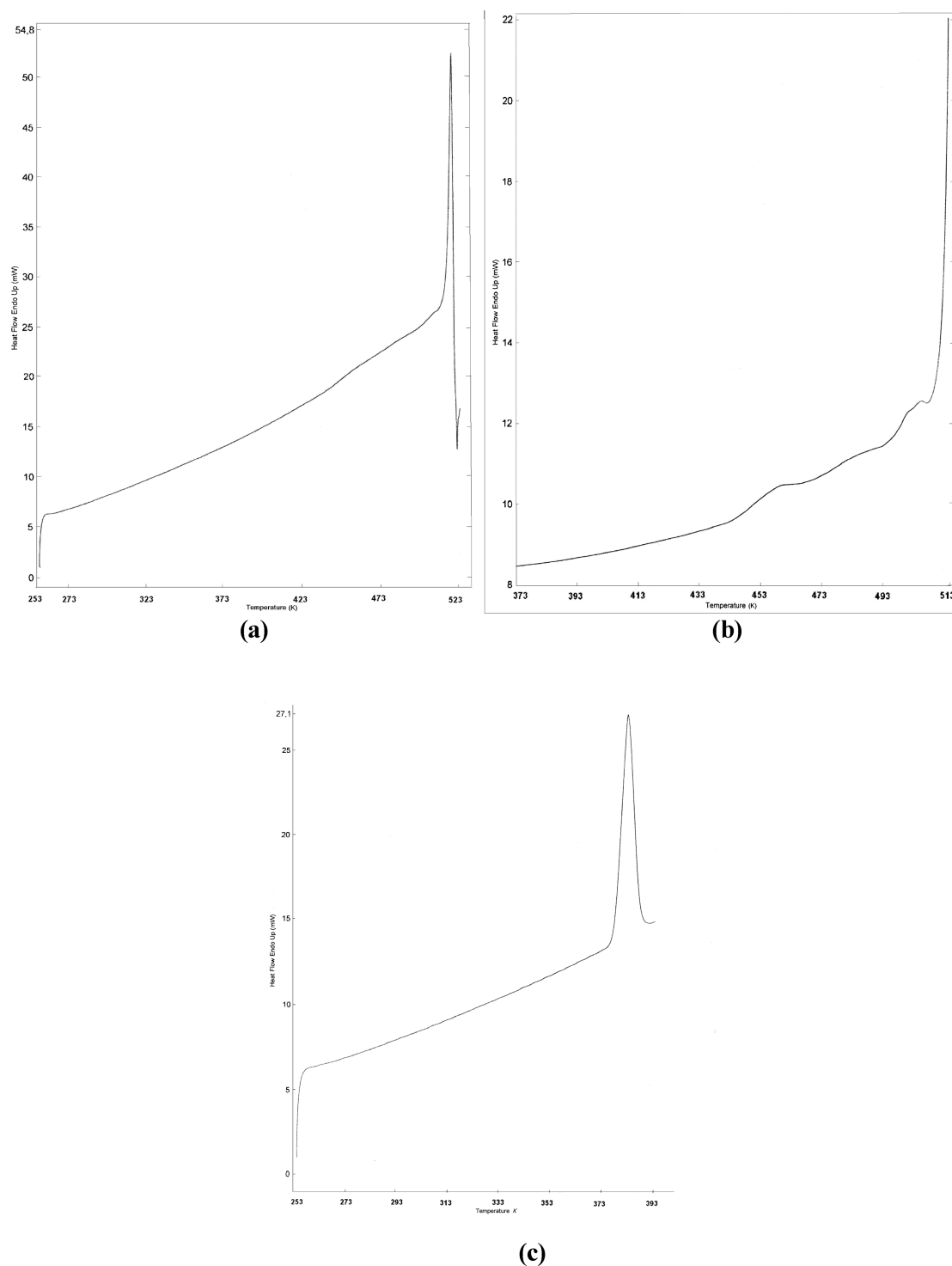
Figure 3. Heat flow as a function of temperature for 2-thiobarbituric acid (a and b) and 1,3-diethyl-2-thiobarbituric acid (c).

the standard deviation of the mean. T_{fus} values are reported as DSC onset temperatures. Also included in the last column of the table is the estimated total phase change entropy, $\Delta_{tpce}S(T_{fus})$.[39] This term includes the total phase change entropy associated in going from $T = 0$ K to the liquid at $T = T_{fus}$. For compounds with phase transitions it represents an estimate of the sum of all entropy changes. For those compounds without any other phase transitions, this entropy change is identical to the fusion entropy.

The total phase change entropies were calculated for the keto tautomer of both 2-thiobarbituric acid and 1,3-diethyl-2-thiobarbituric acid. The rationale for doing so was based on the fact that 2-thiobarbituric acid is converted to the keto form on heating,[4] and at least for this compound, tautomerization is not accompanied by a large enthalpy change as detected by DSC. The lack of appropriate group values was another important consideration. As noted in Table 3, the calculations of $\Delta_{tpce}S(T_{fus})_{calc}$ are

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Table 2. Temperatures and Enthalpies of Solid–Solid Transitions in 2-Thiobarbituric Acid[a]

	first transition			second transition			third transition	
T_{onset}	T_{peak}	$\Delta_{trans}H$	T_{onset}	T_{peak}	$\Delta_{trans}H$	T_{onset}	T_{peak}	$\Delta_{trans}H$
K	K	kJ·mol^{-1}	K	K	kJ·mol^{-1}	K	K	kJ·mol^{-1}
447.2 ± 0.7	458.9 ± 0.4	0.7 ± 0.1	475.8 ± 1.2	483.8 ± 0.7	0.2 ± 0.1	498.0 ± 0.6	503.1 ± 1.8	0.3 ± 0.1

[a] Uncertainties refer to one standard deviation.

Table 3. Temperatures, Enthalpies, and Total Solid–Liquid Phase Change Entropies of Some Barbituric Acids

	T	$\Delta H(T)$	$\Delta S(T)_{expt}$	$\Delta_{tpce}S(T_{fus})^{a}$/J·mol^{-1}·K^{-1}	
	K	kJ·mol^{-1}	J·mol^{-1}·K^{-1}	expt	calcd
2-thiobarbituric acid	447.2 ± 0.7	0.7 ± 0.1	1.6 ± 0.2		
	475.8 ± 1.2	0.2 ± 0.1	0.4 ± 0.2		
	498.0 ± 0.6	0.3 ± 0.1	0.6 ± 0.2		
	516.4 ± 0.1[b]	14.8 ± 0.9	28.7 ± 1.7	31.3 ± 1.7	50
barbituric acid	516.0 ± 0.3[c]	1.3 ± 0.04[c]	2.5 ± 0.1		
	526.4 ± 0.5[c]	20.9 ± 0.14[c]	39.7 ± 0.3	42.2 ± 0.3	50
1,3-diethyl-2-thiobarbituric acid	377.1 ± 0.2	35.5 ± 0.5	94.2 ± 0.5	94.2 ± 0.5	58.6
1,3-diethylbarbituric acid	326.8 ± 0.2[d]	19.6 ± 0.1[d]	60.1 ± 0.3	60.1 ± 0.3	58.6

[a] Experimental values calculated as the sum of each respective entropy change 39; uncertainties refer to one standard deviation. [b] Accompanied by an exothermic decomposition immediately following fusion, Figure 3a; lit.[4] 514.5 K. [c] Reference 20. [d] Reference 24

Table 4. Mean Experimental $C_{p,m}$(cr) Values for 2-Thiobarbituric Acid (1) and 1,3-Diethyl-2-thiobarbituric Acid (2)

T	$C_{p,m}$(cr)/J·mol^{-1}·K^{-1}		T	$C_{p,m}$(cr)/J·mol^{-1}·K^{-1}	
K	1	2	K	1	2
265.15	124.3 ± 4.5	213.5 ± 2.6	350.15	156.6 ± 4.3	273.3 ± 8.3
270.15	126.6 ± 5.0	217.3 ± 2.5	355.15	158.4 ± 4.2	277.8 ± 8.4
273.15	128.0 ± 5.3	219.8 ± 2.3	360.15	160.2 ± 4.0	282.3 ± 8.9
275.15	128.8 ± 5.3	221.2 ± 2.5	365.15	162.6 ± 3.4	287.2 ± 9.3
280.15	131.1 ± 5.5	224.5 ± 2.1	370.15	164.7 ± 3.5	
285.15	132.5 ± 4.8	227.7 ± 2.0	375.15	166.0 ± 4.0	
290.15	134.2 ± 5.3	230.4 ± 2.2	380.15	167.7 ± 4.4	
295.15	136.2 ± 5.6	233.7 ± 2.5	385.15	169.2 ± 4.6	
298.15	137.2 ± 5.7	236.9 ± 2.1	390.15	171.0 ± 4.7	
300.15	138.6 ± 5.1	238.9 ± 3.1	395.15	172.3 ± 4.4	
305.15	140.0 ± 5.9	240.8 ± 2.6	400.15	174.8 ± 4.4	
310.15	142.2 ± 6.1	244.8 ± 3.3	405.15	175.9 ± 4.3	
315.15	144.7 ± 4.7	249.8 ± 4.6	410.15	177.2 ± 4.5	
320.15	146.3 ± 5.0	252.9 ± 4.9	415.15	178.5 ± 4.4	
325.15	147.9 ± 4.2	256.1 ± 7.3	420.15	179.8 ± 3.8	
330.15	150.1 ± 3.9	259.7 ± 7.5	425.15	181.3 ± 3.3	
335.15	152.0 ± 4.0	263.1 ± 7.7	430.15	182.9 ± 3.2	
340.15	153.8 ± 4.2	266.5 ± 8.0			
345.15	155.2 ± 4.5	269.7 ± 7.6			

not in very good agreement with the experiment. The value calculated for 2-thiobarbituric acid is understandably larger than that measured experimentally since the experimental value is probably attenuated by the exothermic decomposition that accompanies fusion. The experimental value for 1,3-diethyl-2-thiobarbituric acid is surprisingly large in comparison to the value

measured for 1,3-diethylbarbituric acid even though both melt at rather similar temperatures. It should be pointed out, however, that based on the crystal structures of the two compounds, 1,3-diethylbarbituric acid is found as the keto tautomer, whereas the 2-thio derivative exists as the corresponding enol.[25,26] Due to the paucity of experimental data on similar thio compounds, the assignment of a new group value to account for this is not currently warranted.

The measured molar heat capacities as a function of temperature for 2-thiobarbituric acid and 1,3-diethyl-2-thiobarbituric acid are collected in Table 4 and Figure 4. The values given in Table 4 are averages of three to six independent runs. The standard deviation of all the data associated with multiple measurements is less than 2 J·mol^{-1}·K^{-1}.

The experimental results for the compounds were fit to a third-order polynomial in temperature of the type:

$$C_{p,m}(cr) = A + B(T/K - 298.15)$$
$$+ C(T/K - 298.15)^2$$
$$+ D(T/K - 298.15)^3 \quad (2)$$

The range studied for each compound, the coefficients of the fitted third-order equation in temperature, and the root-mean-square deviation (rmsd) for both compounds are collected in Table 5. To our knowledge there are no $C_{p,m}$ data in the literature for comparison with our results.

Estimations of $C_{p,m}$(cr)(298.15 K) for both 2-thiobarbituric acid and 1,3-diethyl-2-thiobarbituric acid are listed in Table 6. As with the $\Delta_{tpce}S(T_{fus})_{calc}$ estimations, the same groups used to model the oxo compounds were used to model the corresponding thione derivatives. In this case agreement with experiment is considerably better. For heat capacity measurements, it appears
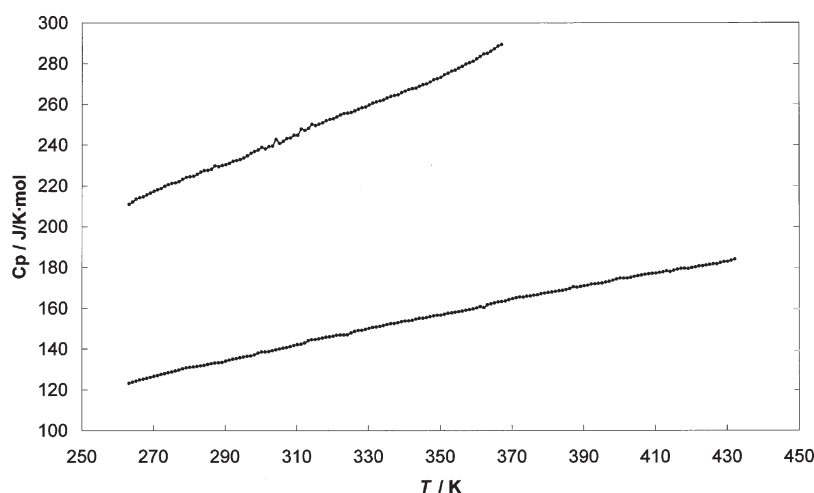
Figure 4. Experimental heat capacities of 2-thiobarbituric (lower line) and 1,3-diethyl-2-thiobarbituric acids (upper line).

Table 5. Coefficients of the Fitted Curves

compound	T K	A $J \cdot mol^{-1} \cdot K^{-1}$	$B \cdot 10^2$ $J \cdot mol^{-1} \cdot K^{-1}$	$C \cdot 10^3$ $J \cdot mol^{-1} \cdot K^{-1}$	$D \cdot 10^5$ $J \cdot mol^{-1} \cdot K^{-1}$	R^2	rmsd[a] $J \cdot mol^{-1} \cdot K^{-1}$
1	265−430	137.6 ± 0.04	38.9 ± 0.2	−0.17 ± 0.04	−13.0 ± 0.03	0.9997	0.3
2	265−365	237.0 ± 0.1	69.2 ± 0.4	−0.31 ± 0.02	1.55 ± 0.29	0.9992	0.6

[a] Root-mean-square deviation.

Table 6. Experimental and Estimated $C_{p,m}(cr)(298.15\ K)$ Values

	$C_{p,m}(cr)(298.15\ K)/J \cdot mol^{-1} \cdot K^{-1}$	
	exptl	calcd
barbituric acid	141.1 ± 0.4[a]	145.1[c]
2-thiobarbituric acid	137.2 ± 5.7[b]	145.1
1,3-diethylbarbituric acid	248.5 ± 7.3[b,c]	246.3[c]
1,3-diethyl-2-thiobarbituric acid	236.9 ± 2.0[b]	246.3

[a] Reference 40 and 41. [b] Uncertainties represent one standard deviation. [c] Reference 24.

that the group values for a cyclic imide $(-C(=O)N(H)C(=O)-)$ and N-substituted cyclic imide $(-C(=O)N(R)C(=O)-)$ can be used for the corresponding monothio derivatives.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Figures of powder diffraction data described in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

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