

Heat capacities of thiane sulfones and thiane sulfoxide Refining of C_p group values for organosulfur compounds and their oxides

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Abstract

A thermophysical study of thiane sulfone, **1**; 1,3-dithiane sulfone, **2**; and 1,3-dithiane sulfoxide, **3** in the temperature intervals between $T = 268$ K and their respective melting temperatures has been carried out. The experimental values for the mole fraction, temperature, enthalpy and entropy of fusion and the associated standard deviation as determined by differential scanning calorimetry (DSC) are $x = (0.9996 \pm 0.0001)$, $T_{\text{fus}} = (370.8 \pm 0.1)$ K, $\Delta_{\text{fus}}H_m = (18.4 \pm 0.2)$ kJ mol⁻¹, $\Delta_{\text{fus}}S_m = (49.6 \pm 0.5)$ J mol⁻¹ K⁻¹ for thiane sulfone, **1**; $x = (0.9994 \pm 0.0001)$, $T_{\text{fus}} = (414.0 \pm 0.2)$ K, $\Delta_{\text{fus}}H_m = (22.0 \pm 0.2)$ kJ mol⁻¹, $\Delta_{\text{fus}}S_m = (53.1 \pm 0.4)$ J mol⁻¹ K⁻¹ for 1,3-dithiane sulfone, **2**; and $x = (0.9977 \pm 0.0001)$, $T_{\text{fus}} = (361.9 \pm 0.1)$ K, $\Delta_{\text{fus}}H_m = (22.6 \pm 0.2)$ kJ mol⁻¹, $\Delta_{\text{fus}}S_m = (62.4 \pm 0.5)$ J mol⁻¹ K⁻¹ for 1,3-dithiane sulfoxide, **3**. Heat capacities in those temperature intervals and in condensed state were measured and no additional solid–solid phase transitions were observed. The heat capacities at $T = 298.15$ K were used to refine group values for organosulfur compounds and their oxides.

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1. Introduction

Over the last few years, we have been involved in a systematic study of the thermodynamic properties of six-membered sulfur-containing heterocycles [1–4]. In this work we present a thermophysical study of the heat capacity behavior of thiane sulfone

(thiacyclohexane-1,1-dioxide, **1**), 1,3-dithiane sulfone (1,3-dithiacyclohexane-1,1-dioxide, **2**); and 1,3-dithiane sulfoxide (1,3-dithiacyclohexane-1-oxide, **3**) as a function of temperature (Fig. 1).

The study was made in the temperature interval between 268 K and the respective melting temperature of each compound. The morphology of the heat capacity curve for each compound was determined within this temperature range.

An objective of this work was to expand the database of available experimental heat capacities of

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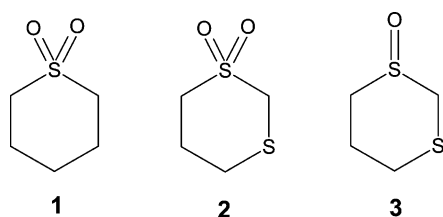


Fig. 1. Thiane sulfone, **1**; 1,3-dithiane sulfone, **2**; and 1,3-dithiane sulfoxide, **3**.

cyclic sulfoxides and sulfones. This data along with other available data from the literature has been used to expand and adjust the group values previously reported for predicting $C_{p,m}$ (c , 298.15 K) of these functional groups [5].

2. Experimental

2.1. Materials

Thiane sulfone was synthesized following the method of Whitehead et al. [6]. The compound was purified by crystallization from hexane–methylene chloride. 1,3-Dithiane sulfoxide was synthesized following the method of Carlson and Helquist [7]. Purification of the desired product was achieved by flash chromatography (hexane–ethyl acetate, 1:9) to obtain the pure sulfoxide. 1,3-Dithiane sulfone was synthesized following the method of Khan et al. [8]. Final purification was accomplished by column chromatography on silica gel (gradient, hexane–ethyl acetate, 9:1 to ethyl acetate) to obtain the pure sulfone. The characterization of both compounds were made by ^1H NMR, ^{13}C NMR, IR and Raman spectroscopies. All samples were carefully dried under vacuum at

50 °C. Determination of purities, assessed by g.c. and DSC by the fractional fusion technique [9] indicated that the mole fraction of impurities in the compounds was less than 0.001 for thiane sulfone, **1**, and for 1,3-dithiane sulfone, **2**, and 0.003 for 1,3-dithiane sulfoxide, **3**.

The samples were studied by DSC over the temperature range $T = 268$ K to their respective melting temperature. No solid–solid phase transitions were observed over this temperature interval.

2.2. Calorimetry

A differential scanning calorimeter (Perkin-Elmer, Pyris 1) equipped with an intra-cooler unit was used. Its temperature and power scales were calibrated [10–12] at heating rates of 0.04 and 0.17 K s $^{-1}$. The temperature scale was calibrated by measuring the melting temperature of the following recommended high-purity reference materials: hexafluorobenzene, benzoic acid, tin, and indium [13]. The power scale was calibrated with high-purity indium (mass fraction: >0.99999) as reference material. Hexafluorobenzene, 99.9% purity, was supplied by Aldrich. Benzoic acid was NIST standard reference sample 39j. Indium and tin reference materials were supplied by Perkin-Elmer. Thermograms of samples hermetically sealed in aluminium pans were recorded in a nitrogen atmosphere. All the pans were weighed before and after the experiments in order to confirm that no product had volatilized. The samples were weighed on a Mettler AT21 microbalance with a sensitivity of 1×10^{-6} g.

After calibration several runs with high-purity benzoic acid and indium as reference materials [13] were performed under the same conditions as the experimental determinations and the results are given in Table 1. The uncertainties of the experimental

Table 1

Comparison between temperatures of fusion T_{fus} and enthalpies of fusion $\Delta_{\text{fus}}H_{\text{m}}$ obtained with our DSC apparatus for two reference materials and their selected values

Compound	Origin	N^a	T_{fus} (K)			$\Delta_{\text{fus}}H_{\text{m}}$ (kJ mol $^{-1}$)		
			This work	Literature	D (T_{fus} , %)	This work	Literature	D ($\Delta_{\text{fus}}H_{\text{m}}$, %)
Benzoic acid	NIST ^b	6	395.7 ± 0.1	395.50 ± 0.02 [13]	0.1	17.78 ± 0.13	18.063 ± 0.042 [13]	−1.6
Indium	Perkin-Elmer	8	430.5 ± 0.1	429.75 ± 0.04 [13]	0.2	3.24 ± 0.10	3.286 ± 0.013 [13]	−1.3

^a Denotes the number of DSC runs.

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Table 2
Heat capacities of α -aluminum oxide (synthetic sapphire) and benzoic acid

T (K)	$C_{p,m}$ (J mol ⁻¹ K ⁻¹)		
	This work	Literature [13]	$D(C_{p,m})$
α -Aluminum oxide			
298.15	78.7 \pm 0.1	79.01	-0.4
300	79.2 \pm 0.1	79.41	-0.3
350	88.5 \pm 0.3	88.84	-0.4
400	95.4 \pm 0.7	96.08	-0.7
Benzoic acid			
280	137.2 \pm 0.6	138.44	-0.9
300	145.3 \pm 0.7	147.64	-1.6
320	155.1 \pm 0.7	156.87	-1.2
350	168.7 \pm 0.8	170.70	-1.2

temperatures and enthalpies of fusion are expressed as the standard deviation of the mean of the experimental values obtained. The accuracies for the temperatures and enthalpies of fusion were calculated

[14] by means of the expressions:

$$D(T_{\text{fus}}) = 10^2 \left[\frac{T_f(\text{exp}) - T_f(\text{lit})}{T_f(\text{lit})} \right] \quad (1)$$

and

$$D(\Delta_{\text{fus}}H_m) = 10^2 \left[\frac{\Delta_{\text{fus}}H_m(\text{exp}) - \Delta_{\text{fus}}H_m(\text{lit})}{\Delta_{\text{fus}}H_m(\text{lit})} \right] \quad (2)$$

as the percentage deviation of the experimental data with regard to the values given in the literature for both temperatures and enthalpies of fusion of benzoic acid and indium, respectively [13].

For determination of purity, melting temperature, and enthalpy of fusion, a heating rate of 0.04 K s⁻¹ was used. For each compound, five to eight samples weighing 1–2 mg were recorded. A fresh sample was used for each run. Although the three organosulfur compounds showed thermal stability in the fusion process, their temperatures and enthalpies of fusion were determined in the fusion peak of fresh samples.

Table 3
Results obtained from DSC measurements for thiane sulfone; 1,3-dithiane sulfone; and 1,3-dithiane sulfoxide

m (mg)	x ($\times 10^2$)	T_{fus} (K)	$\Delta_{\text{fus}}H_m$ (kJ mol ⁻¹)	$\Delta_{\text{fus}}S_m$ (J mol ⁻¹ K ⁻¹)
Thiane sulfone				
1.127	99.95	371.0	18.2	49.1
1.505	99.96	370.7	18.9	51.0
1.211	99.96	370.7	18.8	50.7
1.608	99.98	371.0	17.9	48.2
1.230	99.97	370.8	18.1	48.8
Mean values \pm standard deviation of the mean	99.964 \pm 0.005	370.8 \pm 0.1	18.4 \pm 0.2	49.6 \pm 0.5
1,3-Dithiane sulfone				
2.060	99.95	414.4	22.3	53.8
1.105	99.94	414.5	21.5	51.9
1.656	99.93	413.6	22.5	54.4
1.400	99.95	413.8	21.8	52.7
1.595	99.93	413.8	21.9	52.9
Mean values \pm standard deviation of the mean	99.940 \pm 0.004	414.0 \pm 0.2	22.0 \pm 0.2	53.1 \pm 0.4
1,3-Dithiane sulfoxide				
1.925	99.78	361.9	22.4	61.9
1.232	99.78	361.8	22.8	63.0
1.548	99.75	361.9	22.6	62.4
2.135	99.72	362.3	23.2	64.0
1.529	99.80	361.7	22.0	60.8
Mean values \pm standard deviation of the mean	99.766 \pm 0.010	361.9 \pm 0.1	22.6 \pm 0.2	62.4 \pm 0.5

The term m refers to the mass of each experiment, x refers to the purity in mole fraction, T_{fus} is the temperature of fusion, $\Delta_{\text{fus}}H_m$ the molar enthalpy of fusion, and $\Delta_{\text{fus}}S_m$ is the molar entropy of fusion.

Heat capacities were determined by the “scanning method” following the experimental methodology previously described [14–17] and using synthetic sapphire (α -aluminium oxide) as reference material [13–15]. For heat capacity determinations, four to six samples weighing 10–25 mg were scanned for each compound in the temperature range from 268 K to its melting temperature using a heating rate of 0.17 K s^{-1} . In order to check the experimental method followed, heat capacity experiments with benzoic acid and synthetic sapphire as reference materials [13] in the temperature intervals $T = 268\text{--}360$, and $268\text{--}410 \text{ K}$, respectively were made. Table 2 gives the mean values for heat capacity determinations at

the selected temperatures and their uncertainties expressed as the standard deviations of the mean. A comparison of our results with those reported in the literature [13] is also given.

The quantity $D(C_{p,m})$ defined as:

$$D(C_{p,m}) = 10^2 \left[\frac{C_{p,m}(\text{exp}) - C_{p,m}(\text{lit})}{C_{p,m}(\text{lit})} \right] \quad (3)$$

gives the accuracy [14] of our measurements for the selected temperatures.

The temperature intervals where heat capacities of thiane sulfone, 1,3-dithiane sulfone and 1,3-dithiane sulfoxide were measured are: $T = 268\text{--}369$ for thiane

Table 4

Molar heat capacities of crystalline thiane sulfone; 1,3-dithiane sulfone; and 1,3-dithiane sulfoxide

T (K)	$C_{p,m}$ ($\text{J mol}^{-1} \text{K}^{-1}$)	T (K)	$C_{p,m}$ ($\text{J mol}^{-1} \text{K}^{-1}$)	T (K)	$C_{p,m}$ ($\text{J mol}^{-1} \text{K}^{-1}$)
Thiane sulfone					
268.15	144.0	295.15	157.9	325.15	172.6
270.15	145.1	298.15	159.4	330.15	175.3
273.15	146.6	300.15	160.4	335.15	178.2
275.15	147.4	305.15	162.6	340.15	181.8
280.15	150.0	310.15	165.0	345.15	185.8
285.15	152.7	315.15	167.3	350.15	188.5
290.15	155.3	320.15	169.7	355.15	192.5
$C_{p,m}$ ($\text{J mol}^{-1} \text{K}^{-1}$) = $0.0013T$ (K) ² - $0.2989T$ (K) + 128.84, $R^2 = 0.9983$					
1,3-Dithiane sulfone					
268.15	142.4	310.15	162.1	365.15	186.6
270.15	144.1	315.15	164.1	370.15	189.8
273.15	146.1	320.15	166.4	375.15	191.9
275.15	146.9	325.15	168.7	380.15	193.7
280.15	149.1	330.15	171.2	385.15	195.6
285.15	150.9	335.15	173.3	390.15	199.5
290.15	153.5	340.15	174.8	395.15	203.3
295.15	155.7	345.15	176.4	400.15	206.4
298.15	157.6	350.15	178.9	405.15	209.3
300.15	158.1	355.15	181.7	408.15	212.0
305.15	159.4	360.15	184.2		
$C_{p,m}$ ($\text{J mol}^{-1} \text{K}^{-1}$) = $0.0007T$ (K) ² - $0.013T$ (K) + 97.849, $R^2 = 0.9987$					
1,3-Dithiane sulfoxide					
268.15	135.3	295.15	146.1	325.15	158.6
270.15	136.0	298.15	147.6	330.15	160.8
273.15	137.3	300.15	148.1	335.15	163.1
275.15	138.2	305.15	150.1	340.15	165.8
280.15	140.3	310.15	152.4	345.15	168.7
285.15	142.3	315.15	154.6	348.15	170.4
290.15	144.3	320.15	156.7		
$C_{p,m}$ ($\text{J mol}^{-1} \text{K}^{-1}$) = $0.0009T$ (K) ² - $0.149T$ (K) + 108.38, $R^2 = 0.9991$					

sulfone, **1**; $T = 268\text{--}410\text{ K}$ for 1,3-dithiane sulfone, **2**; and $T = 268\text{--}358\text{ K}$ for 1,3-dithiane sulfoxide, **3** and the standard deviations of the mean at $T = 298.15\text{ K}$ were ± 0.13 for thiane sulfone, **1**, ± 0.61 for 1,3-dithiane sulfone, **2** and $\pm 0.41\text{ J mol}^{-1}\text{ K}^{-1}$ for 1,3-dithiane sulfoxide, **3**.

3. Results and discussion

The mass, mole fraction, experimental values of the fusion temperature and enthalpy and the calculated entropy of fusion of each experiment are given in Table 3. The mean value and standard deviation of the mean is included as the last entry for each compound studied.

The mean values of the heat capacity measurements and equations of $C_{p,m}(T)$ for the three compounds studied are given in Table 4; the experimental heat capacity curves are shown in Fig. 2. Heat capacity values at $T = 298.15\text{ K}$ of 159.4, 157.6, and $147.6\text{ J mol}^{-1}\text{ K}^{-1}$ have been measured for thiane sulfone, 1,3-dithiane sulfone and 1,3-dithiane sulfoxide, respectively.

Heat capacities at 298.15 K have proven quite useful in adjusting vaporization, sublimation and fusion enthalpies with temperature. Although the individual heat capacities of liquids, solids and gases differ, each is a function of temperature. For most compounds, heat capacity curves of each phase have a tendency to parallel each other as a function of temperature. Consequently, the use of $\Delta C_{p,m}(298.15\text{ K})$ values are useful in adjusting phase change enthalpies for temperature and equations for doing this have been reported [18,19]. With the exception of compounds that are gases at 298.15 K, the gas phase heat capacity of most substances needs to be estimated. Similarly, in adjusting fusion enthalpies from the melting temperature to $T = 298.15\text{ K}$, the liquid phase heat capacity must be estimated. These temperature adjustments requiring heat capacities are necessary refinements when converting phase change enthalpies to the standard state [18].

Group values for adjusting the hydrocarbon portion of a molecule are given in Table 5. Group values for the hydrocarbon portion of the molecule are identical to those reported previously [5] with the exception of the value for an internal quaternary aromatic sp^2

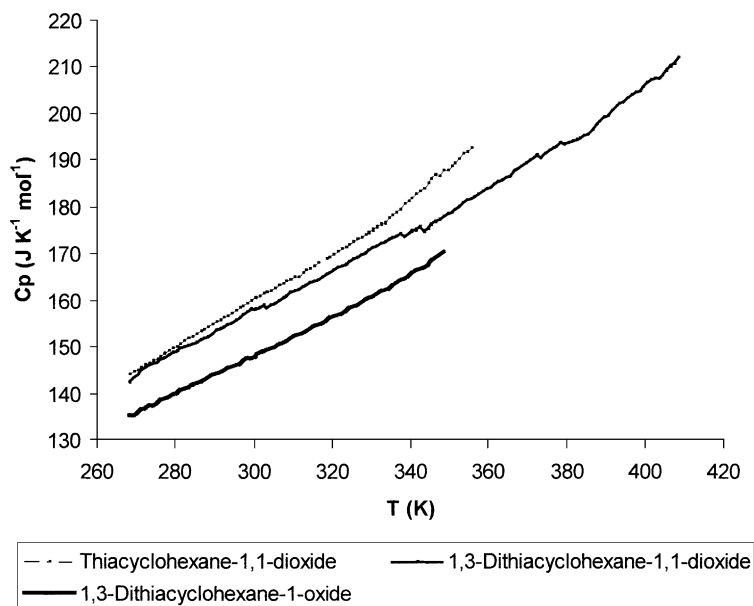


Fig. 2. Experimental heat capacities of thiacyclohexane-1,1-dioxide (dotted line); 1,3-dithiacyclohexane-1,1-dioxide (thin line); 1,3-dithiacyclohexane-1-oxide, (thick line).

Table 5

Hydrocarbon group values for liquids, Γ_1 , and solids, Γ_c

Hydrocarbon group	Γ_1 (J mol ⁻¹ K ⁻¹)	Γ_c (J mol ⁻¹ K ⁻¹)
Primary sp ³ carbon	34.9	36.6
Secondary sp ³ carbon	31.9	26.9
Tertiary sp ³ carbon	22.4	9
Quaternary sp ³ carbon	14	-5
Secondary sp ² carbon	25.8	46
Tertiary sp ² carbon	27.8	21.4
Quaternary sp ² carbon	21.7	6.9
Tertiary sp carbon	34.3	37.1
Quaternary sp carbon	28.9	15.5
Tertiary aromatic sp ² carbon	21.8	17.5
Quaternary aromatic sp ²	15.3	8.5
Internal quaternary aromatic sp ² carbon ^a	16	9.1
Cyclic secondary sp ³ carbon	25.9	24.6
Cyclic tertiary sp ³ carbon	20.6	11.7
Cyclic quaternary sp ³ carbon	18	6.1
Cyclic tertiary sp ²	21.8	15.9
Cyclic quaternary sp ²	21.2	4.7

^a These group values have recently been changed from the value reported previously [20].

carbon such as found in coronene. The value for this group has recently been modified [20].

Table 6 lists auxiliary group values used in conjunction with the values in Table 5 to evaluate the group values listed in Table 7. Previous values for a sulfone and cyclic sulfide were tentatively based on only a single experimental heat capacity value. The value

Table 6

Functional group values for liquids Γ_1 and/or solids Γ_c used in this study

Functional group	Γ_1 (J mol ⁻¹ K ⁻¹)	Γ_c (J mol ⁻¹ K ⁻¹)
Carboxylic acid	87.4	53.1
Cyclic ether	24.6	9.7
Primary sp ³ nitrogen	59.4	21.6
Chlorine	30.8	28.7

Table 7

Heat capacity contributions of functional groups, Γ_c , evaluated in this study^a

Functional group	Γ_c (J mol ⁻¹ K ⁻¹)	Number of compounds
Cyclic sulfide	18.2	13
Cyclic sulfoxide	[31]	1
Cyclic sulfone	[38.7]	2
Sulfone	[52.4]	5

^a Values in square brackets are considered to be tentative assignments.

for a cyclic sulfide changed slightly from 20.3 to 18.2 but is now based on a more statistically significant number of experimental data. The value for a sulfone, also previously based on a single experimental value, changed significantly from 88.7 to 52.4 J mol⁻¹ K⁻¹. This value, based now on five data points, is still considered tentative. Group values for cyclic sulfoxides and cyclic sulfones are new. Since they are based on only a few experimental measurements, they are still considered to be tentative assignments.

The new assignments are based on the data reported in Table 8. The values were obtained by varying the group values until the following function was minimized:

$$\left[\frac{C_{p,m}(c, \text{exp}) - C_{p,m}(c, \text{calc})}{C_{p,m}(c, \text{exp})} \right]^2 \quad (4)$$

The calculated and experimental values and the method of estimation are given in Table 8. The correlation was characterized by a standard deviation of ± 15 J mol⁻¹ K⁻¹. A linear regression of the experimental versus calculated values resulted in the following linear relationship:

$$\begin{aligned} C_{p,m}(c, 298.15 \text{ K})_{\text{exp}} \\ = (1.05 \pm 0.06)C_{p,m}(c, 298.15 \text{ K})_{\text{calc}} \\ - (4.7 \pm 15.8); \quad r^2 = 0.949 \end{aligned} \quad (5)$$

Table 8

Compounds used to evaluate the group values reported in Table 7

Compound	Experimental $C_{p,m}$ (<i>c</i> , 298.15 K)	Calculated $C_{p,m}$ (<i>c</i> , 298.15 K)	Calculation
C ₂ H ₆ O ₂ S, dimethyl sulfone ^a	125.3	125.6	2 × 36.6 + 52.4
C ₃ H ₆ S ₃ , 1,3,5-trithiane ^b	135.3	128.4	3 × 24.6 + 3 × 18.2
C ₄ H ₈ OS ₂ , 1,3-dithiane sulfoxide ^c	147.6	147.6	4 × 24.6 + 18.2 + 31
C ₄ H ₈ O ₂ S ₂ , 1,3-dithiane sulfone ^c	157.6	155.3	4 × 24.6 + 18.2 + 38.7
C ₄ H ₈ S ₂ , 1,3-dithiane ^a	110.4	134.8	4 × 24.6 + 2 × 18.2
C ₄ H ₈ S ₂ , 1,4-dithiane ^a	122.5	134.8	4 × 24.6 + 2 × 18.2
C ₄ H ₁₀ O ₆ S ₃ , tris(methylsulfonyl)methane ^a	269.7	278.4	3 × 36.6 + 3 × 52.4 + 9
C ₅ H ₄ O ₂ S, 2-thiophene carboxylic acid ^d	142.0	123.7	3 × 15.9 + 4.7 + 53.1 + 18.2
C ₅ H ₄ O ₂ S, 3-thiophene carboxylic acid ^d	134.1	123.7	3 × 15.9 + 4.7 + 53.1 + 18.2
C ₅ H ₁₀ O ₂ S, thiane sulfone ^c	159.4	161.7	5 × 24.6 + 38.7
C ₈ H ₁₂ S ₆ , 1,3,5,7-tetramethyl-2,4,6,8,9,10-hexathiaadamantane ^a	301.6	280.0	4 × 36.6 + 4 × 6.1 + 6 × 18.2
C ₁₀ H ₁₆ S ₄ , 1,3,5,7-tetramethyl-2,4,6,8-tetra-thiaadamantane ^a	295.9	292.8	4 × 36.6 + 2 × 24.6 + 4 × 6.1 + 4 × 18.2
C ₉ H ₁₄ S, 2-thiaadamantane ^a	213.0	188.0	5 × 24.6 + 4 × 11.7 + 18.2
C ₁₂ H ₈ OS, phenoxathin ^a	213.8	201.9	8 × 17.5 + 4 × 8.5 + 18.2 + 9.7
C ₁₂ H ₈ S, dibenzothiophene ^a	196.5	192.2	8 × 17.5 + 4 × 8.5 + 18.2
C ₁₂ H ₈ S ₂ , thianthrene ^a	222.6	210.4	8 × 17.5 + 4 × 8.5 + 2 × 18.2
C ₁₂ H ₁₀ O ₂ S, diphenyl sulfone ^a	244.3	244.4	10 × 17.5 + 2 × 8.5 + 52.4
C ₁₂ H ₁₂ N ₂ O ₂ S, 4,4'-diaminodiphenyl-sulfone ^a	314.9	269.6	8 × 17.5 + 4 × 8.5 + 2 × 21.6 + 52.4
C ₁₂ H ₈ Cl ₂ O ₂ S, 4,4'-dichlorodiphenyl-sulfone (Dapsone) ^a	269.3	283.8	8 × 17.5 + 4 × 8.5 + 2 × 28.7 + 52.4

Values in J mol⁻¹ K⁻¹.^a See [21].^b See [22].^c This work.^d See [23].

4. Summary

A study of the thermal behavior of thiane sulfone, **1**; 1,3-dithiane sulfone, **2**; and for 1,3-dithiane sulfoxide, **3** is reported as a function of the temperature. Experimental values for the mole fraction, temperature, enthalpy and entropy of fusion and the associated standard deviation as determined by DSC are $x = (0.9996 \pm 0.0001)$, $T_{\text{fus}} = (370.8 \pm 0.1)$ K, $\Delta_{\text{fus}}H_m = (18.4 \pm 0.2)$ kJ mol⁻¹, $\Delta_{\text{fus}}S_m = (49.6 \pm 0.5)$ J mol⁻¹ K⁻¹ for thiane sulfone, **1**; $x = (0.9994 \pm 0.0001)$, $T_{\text{fus}} = (414.0 \pm 0.2)$ K, $\Delta_{\text{fus}}H_m = (22.0 \pm 0.2)$ kJ mol⁻¹, $\Delta_{\text{fus}}S_m = (53.1 \pm 0.4)$ J mol⁻¹ K⁻¹ for 1,3-dithiane sulfone, **2**; and $x = (0.9977 \pm 0.0001)$, $T_{\text{fus}} = (361.9 \pm 0.1)$ K, $\Delta_{\text{fus}}H_m = (22.6 \pm 0.2)$ kJ mol⁻¹, $\Delta_{\text{fus}}S_m = (62.4 \pm 0.5)$ J mol⁻¹ K⁻¹ for 1,3-dithiane sulfoxide, **3**.

No additional solid–solid phase transition was found for any of the compounds over the temperature range examined. The heat capacity of these three organosulfur compounds were also evaluated from $T = 268$ K to their respective melting points. Values of their heat capacities along with other literature values were used to refine existing group values for sulfur and its oxides in several different environments.

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