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Phase transitions properties of *N*,*N*-dimethyl-4-nitroaniline

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Abstract

The present work reports an experimental study aiming to determine several thermodynamic properties of fusion and sublimation of the chromophore *N*,*N*-dimethyl-4-nitroaniline. This compound is commonly used as a reference in studies focused on the non-linear optical (NLO) characteristics of chromophores. Using the Knudsen mass-loss effusion method, the vapor pressures of the crystalline phase of *N*,*N*-dimethyl-4-nitroaniline were measured over the temperature range between 341.1 K and 363.5 K. The standard molar enthalpy, entropy, and Gibbs energy of sublimation were calculated from the experimental results, at 298.15 K, and compared with those given in the literature. Differential scanning calorimetry was used to determine the temperature and enthalpy of fusion, as well as the isobaric heat capacities of the crystalline compound under study. Additionally, the enthalpic and entropic contributions to *N*,*N*-dimethyl-4-nitroaniline's volatility were assessed, and it was determined that is greatly conditioned by enthalpic factors.

Author Keywords. *N*,*N*-dimethyl-4-nitroaniline, Vapor pressures, Phase transitions, Sublimation, Fusion, Heat capacities

Type: Research Article

Introduction

N,*N*-dimethyl-4-nitroaniline (4DMNA) is an organic chromophore used as a reference compound in the study of non-linear optical (NLO) properties of chromophores (Borbulevych et al. 2002). This choice stems from its significant bathochromic shift that enables the analysis of electrostatic interactions between the molecule and the surrounding medium (Nakano 2015). This property makes 4DMNA suitable for potential applications in the field of telecommunications, optical data storage, and information processing (Zhang, Cao, and Guo 2012). It is also known for its piezoelectric properties due to the flexible crystal matrix that crystallizes on an acentric structure, and also for the high molecular dipole moment. The 4DMNA crystals exhibit super elasticity (Baptista et al. 2022), which refers to the material's ability to respond to applied stress (Ramezannejad, Xu, and Qian 2018). Additionally, they display super plasticity (Baptista et al. 2022) characterized by the capacity to undergo significant tensile deformations without necking or fracturing (Perez-Prado and Kassner 2015).

These unique properties allow for the preservation of single crystallinity during deformation, making them promising for potential applications in photonics and bioelectronics (Baptista et al. 2022). Furthermore, it is possible to study the impact of the intra- and/or intermolecular photoreduction process induced by the initiator in the generation of free radicals thanks to the bifunctional nature of 4DMNA, which has an electron donor and acceptor group in the same molecule. This increases the effectiveness of this bimolecular system as a photoinitiator of polymerization (Costela et al. 2001).

Despite the compound's significance, certain of its thermodynamic properties are unknown or need further research. Particularly, accurate and trustworthy information about vapor pressures and related sublimation properties and fusion is scarce. In this way, it was decided to perform a thermodynamic study on the sublimation of 4DMNA through vapor pressure measurements at different temperatures, using the Knudsen mass-loss effusion method. It is mainly used for measuring vapor pressures of pure substances in the crystalline phase, in the interval between (0.1 and 1) Pa, and it has been used by our research group for years (Ribeiro da Silva, Monte, and Santos 2006; Ribeiro da Silva et al. 2010; Almeida et al. 2012; Monte, Almeida, and Notario 2018). From (p,T) experimental results, the standard molar enthalpy, entropy and Gibbs energies of sublimation of 4DMNA were calculated, at 298.15 K. These results were compared with those reported before in the literature for this compound (Acree et al. 1994; Murata, Sakiyama, and Seki 1985; Stephenson and Malanowski 1987; Furukawa et al. 1984), enabling to observe certain inconsistencies in the values previously published. The sublimation results reported in the literature for 4DMNA, were determined calorimetrically (Furukawa et al. 1984; Murata, Sakiyama, and Seki 1985) as well as through the dependance of vapor pressure on temperature (Acree et al. 1994; Stephenson and Malanowski 1987).

Additionally, a calorimetric study using differential scanning calorimetry was carried out to determine the temperature and enthalpy of fusion, as well as the isobaric heat capacities of the crystalline 4DMNA. To the best of our knowledge, these last two properties were for the first time determined experimentally for *N,N*-dimethyl-4-nitroaniline. By considering the thermodynamic properties of sublimation determined in this study, the impact of both enthalpic and entropic factors on the volatility of this compound was evaluated using the well-known relation $\Delta_{\mathrm{cr}}^{\mathrm{g}}G_{\mathrm{m}}^{\mathrm{o}}(\theta)=\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(\theta)-\theta\cdot\Delta_{\mathrm{cr}}^{\mathrm{g}}S_{\mathrm{m}}^{\mathrm{o}}(\theta)$. It was found that the volatility is significantly influenced by the enthalpic term.

This research work is part of a larger project aimed at the determination and estimation of thermodynamic properties of phase transitions of benzene-derived compounds (Almeida and Monte 2013; Almeida et al. 2019; 2022).

1. Materials and Methods

1.1. N,N-dimethyl-4-nitroaniline

The compound studied was commercially acquired from *Alfa Aesar* with a certified purity degree of 0.996. Since the original purity degree is lower than the required for this study, the compound was further purified through sublimation under reduced pressure before the experimental determinations. The purity of both the purchased compound and the purified sample was evaluated using gas-liquid chromatography performed on an Agilent 4890D chromatograph, equipped with a non-polar capillary HP-5 column, a flame ionization detector (FID), and nitrogen as the carrier gas. The solvent used for the chromatography analysis was dimethylformamide. The Karl Fischer’s coulometric titration was used to determine the water content of the purified sample, using a Methrom titration system consisting of an 831

Coulometer equipped with a generator electrode (without a diaphragm) and using HYDRANAL™ as the reagent. Table 1 details the information on purity and methods of purification and analysis of 4DMNA.

Compound	**CASNR**	**Source**	**Minimum initial purity**[a]	**Purification Method**	**Final mass fraction purity**	**Analysis method**[b] (dry basis)	**% Water content**[c]
N,*N*-dimethyl-4-nitroaniline	100-23-2	Alfa Aesar	0.996	Sublimation under reduced pressure	0.9987	GC (FID)	0.04 ± 0.01

[a]As stated in the certificate of analysis from the manufacturer. [b]Gas-liquid chromatography with flame ionization detector. [c]Determined using Karl Fisher coulometric titration (mass percentage). The error was assigned as the standard deviation of three independent measurements.

Table 1: Source, purity, and methods of purification and analysis of *N*,*N*-dimethyl-4-nitroaniline.

1.2. Thermal Analysis

1.2.1. Differential Scanning Calorimetry

1.2.2. Thermodynamic properties of Fusion

The samples of the purified compound were analyzed in a Netzsch heat flow calorimeter (model 204 F1 *Phoenix*), allowing the determination of the onset temperature and enthalpy of fusion and the confirmation of the absence of phase transitions in the 4DMNA crystalline phase. The samples were sealed in hermetic aluminum crucibles and subjected to two heating-cooling cycles in order to examine the possible existence of phase transitions. At least four independent runs were performed at a heating rate of 2.0 K.min^{-1}, from T = 293 K to a temperature (20 to 25) K higher than its temperature of fusion. A controlled nitrogen flux was used as a purge and protective gas, preventing an eventual contamination of the calorimeter. The temperature and heat flow scales of the calorimeter were calibrated using four substances from Netzsch's kit (Netzsch 2022): indium (I-2803), tin (S-2776), bismuth (B-3067), and adamantane (A-2838), and using another six high-purity reference compounds (Sabbah and Watik 1992; Sabbah et al. 1999; Della Gatta et al. 2006; Roux et al. 2008; Chang and Bestul 1972): *o*-terphenyl, naphthalene, benzoic acid, cyclohexane, biphenyl and triphenylene. The standard uncertainties derived from the calibration results are $u(T/\text{K})$ = 0.46 and $u\{\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\text{o}}(T_{\text{fus}})/\text{kJ·mol}^{-1}\}$ = 0.21. Before melting, no crystalline phase transitions or signals of decomposition were observed under the experimental conditions used.

1.2.3. Crystalline Heat Capacities

The crystalline heat capacity measurements were conducted in this work in the temperature range between 291.4 K and 409.7 K, using Netzsch's recommended procedures, in accordance with ASTM E1269, DIN 51 007, and ISO 11357-4 standards. The temperature program used consisted of an isothermal step of 25 minutes at the initial temperature, a temperature ramp of 10 K·min^{-1}, and a second isothermal step of 25 minutes at the final temperature. Nitrogen was used as purge and protective gas with flow rates of 30 cm^{3}·min^{-1} and 50 cm^{3}·min^{-1}, respectively. Each heat capacity measurement included three runs: blank, calibration standard (sapphire), and sample studied. To verify the reliability of the experimental technique, heat capacity experiments were performed using benzoic acid (Furukawa, McCoskey, and King 1951) and synthetic sapphire as reference materials. The relative percentage error of the calibration measurements was less than 2 % compared to literature values. The temperature interval used for the calibration measurements was between 281 K and 370 K. The aluminum crucibles were used to hold the samples, which were weighed with a precision of ± 0.1 µg on a Mettler Toledo balance (model UMT2), and the crucible lids were left unsealed during the measurements.

1.3. Vapor Pressure Measurements

1.3.1. Knudsen mass-loss effusion method

Using a Knudsen mass-loss effusion apparatus capable of operating with nine effusion cells simultaneously, the vapor pressures of the crystalline phase of 4DMNA were measured at different temperatures. The effusion technique setup and procedure were previously described and tested (Ribeiro da Silva, Monte, and Santos 2006). In a typical experiment, effusion cells with different effusion orifice areas are placed in cylindrical holes in three aluminum blocks, each maintained at a constant temperature (different for each block). The effusion orifices were manufactured (Goodfellow™) on platinum foil of (0.0125 ± 0.001) mm thickness, with the corresponding areas (Almeida, Oliveira, and Monte 2015) and Clausing factors reported in Table 2:

Orifices	**Area/mm^2 ^{a}**	**w_o^{b}**
A_1	0.636 ± 0.004	0.986
A_2		
A_3		
B_1	0.785 ± 0.004	0.988
B_2		
B_3		
C_1	0.985 ± 0.004	0.989
C_2		
C_3		

[a] The uncertainties were calculated by the Root Sum Square (RSS) method;

[b] $w_o = 1/\{1 + (l/2r)\}$, where l is the thickness of the platinum foil and r is the radius of the orifices.

Table 2: Effusion cells orifices areas and respective Clausing factors.

The mass loss of the sample due to the effusion process, *m*, was determined for each effusion experiment by weighing the effusion cells before and after the effusion period, *t*, with an estimated uncertainty of 1×10^{-5} g. Using Equation (1), the vapor pressure *p* of the crystalline sample in each effusion cell was calculated at the temperature *T*,

$$p = \frac{m}{A_o w_o t}\left(\frac{2\pi RT}{M}\right)^{0.5} \tag{1}$$

where the molar mass of the effusing vapor is represented by *M*, and the molar gas constant by *R* (with a value of 8.3144598 J·K^{-1}·mol^{-1} (Mohr et al 2016)). The standard uncertainties for the temperature and vapor pressure measurements were determined to be u = 0.01 K and u = 0.02 Pa.

2.4. Computational details

Gaussian 09 software package (Frisch et al. 2010) was applied to conduct ab initio molecular orbital calculations on *N*,*N*-dimethyl-4-nitroaniline, employing the G3(MP2)//B3LYP composite method (Baboul et al. 1999). This approach is derived from the Gaussian-3 (G3) theory (Curtiss et al. 1998), incorporating the B3LYP density functional method for optimizing geometries and considering zero-point energies. A comprehensive description of this method can be found in the referenced literature (Baboul et al. 1999).

2. Discussion

Table 3 reports the results of the onset temperatures, T_{fus}, molar enthalpies $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{\mathrm{o}}(T_{\mathrm{fus}})$ and entropies $\Delta_{\mathrm{cr}}^{\mathrm{l}}S_{\mathrm{m}}^{\mathrm{o}}(T_{\mathrm{fus}})$ of fusion of 4DMNA determined using DSC, and also the available literature result of T_{fus}. To the best of our knowledge, no fusion enthalpy values have been reported before for this compound.

Exp.	**T_{fus}(onset)/K**	$\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{\mathrm{o}}(T_{\mathrm{fus}})$ **/kJ·mol^{-1}**	$\Delta_{\mathrm{cr}}^{\mathrm{l}}S_{\mathrm{m}}^{\mathrm{o}}(T_{\mathrm{fus}})$ **/J·K^{-1}·mol^{-1}**
1	435.45	27.23	62.5
2	435.04	27.14	62.4
3	435.26	27.75	63.8
4	435.26	27.35	62.8
Mean	435.25 ± 0.46[a]	27.37 ± 0.20[a]	62.9 ± 0.5[b]
Literature	436.9 (Campbell 1949)		

[a]The reported experimental uncertainties were determined from the combined standard uncertainties (which include the standard deviation of the mean of the four experimental runs and the standard uncertainty of the differential scanning calorimeter calibration). [b]Uncertainties calculated through the RSS method.

Table 3: Temperatures, molar enthalpies, and entropies of fusion of the compound studied.

Information about the effusion vapor pressures determined using the Knudsen mass-loss effusion technique is reported in Table 4. The values included in this table correspond to the mean vapor pressure data derived from individual cells at a certain temperature.

***T*/K**	341.12	343.25	345.59	347.11	349.14	351.25	353.47	355.11	357.24	359.45	361.61	363.50
<*p*>/Pa	0.112	0.140	0.177	0.213	0.263	0.318	0.404	0.479	0.593	0.729	0.897	1.083

[a] For each temperature, the presented vapor pressures are the mean of the results obtained with three different effusion orifices.

Table 4. Effusion vapor pressure results for crystalline *N*,*N*-dimethyl-4-nitroaniline[a]

The experimental (p,T) data, determined in this study using the Knudsen effusion method, were fitted by the truncated form of Clarke-Glew equation, Equation (2), (Clarke and Glew 1966), enabling to obtain a variety of thermodynamic properties of sublimation such as standard molar enthalpy, $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$, entropy, $\Delta_{\mathrm{cr}}^{\mathrm{g}}S_{\mathrm{m}}^{\mathrm{o}}$ (calculated using Equation (3)), and Gibbs energy $\Delta_{\mathrm{cr}}^{\mathrm{g}}G_{\mathrm{m}}^{\mathrm{o}}$. Table 5 reports the results of these properties for 4DMNA and their associated uncertainties, as well as the values of vapor pressures calculated for two different temperatures, using Equation (2).

$$R\ln\left(\frac{p}{p^{\mathrm{o}}}\right)=-\frac{\Delta_{\mathrm{cr}}^{\mathrm{g}}G_{\mathrm{m}}^{\mathrm{o}}(\theta)}{\theta}+\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(\theta)\left(\frac{1}{\theta}-\frac{1}{T}\right)+\Delta_{\mathrm{cr}}^{\mathrm{g}}C_{p,\mathrm{m}}^{\mathrm{o}}(\theta)\left[\left(\frac{\theta}{T}\right)-1+\ln\left(\frac{T}{\theta}\right)\right] \qquad (2)$$

In the Equation (2), p^o is the selected reference pressure, in this work ($p^o = 10^5$ Pa), p is the vapor pressure at temperature T, θ is the reference temperature (in this work, unless stated otherwise θ = 298.15 K) and R is the molar gas constant.

$$\Delta_{\mathrm{cr}}^{\mathrm{g}} S_{\mathrm{m}}^{\mathrm{o}}(\theta) = \frac{\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^{\mathrm{o}}(\theta) - \Delta_{\mathrm{cr}}^{\mathrm{g}} G_{\mathrm{m}}^{\mathrm{o}}(\theta)}{\theta} \tag{3}$$

Δ*T*	**ϑ**	$\Delta_{\mathrm{cr}}^{\mathrm{g}} G_{\mathrm{m}}^{\mathrm{o}}(\theta)^{\mathrm{a}}$	p^{b}	$\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^{\mathrm{o}}(\theta)^{\mathrm{a}}$	$\Delta_{\mathrm{cr}}^{\mathrm{g}} S_{\mathrm{m}}^{\mathrm{o}}(\theta)^{\mathrm{c}}$	R^2	$-\Delta_{\mathrm{cr}}^{\mathrm{g}} C_{p,\mathrm{m}}^{\mathrm{o}}(\theta)^{\mathrm{a}}$	$\sigma_{\mathrm{r}}^{\mathrm{d}}$
K	K	kJ·mol⁻¹	Pa	kJ·mol⁻¹	J·K⁻¹·mol⁻¹		J·K⁻¹·mol⁻¹	
				***Crystalline phase* (Knudsen effusion method)**				
341.1 to 363.5	298.15	47.27 ± 0.12	$5.23 \cdot 10^{-4}$	106.0 ± 0.8	197.0 ± 2.7	0.9998	25.8 ± 6.7$^{\mathrm{e}}$	0.0092
	352.31$^{\mathrm{f}}$	36.72 ± 0.02	0.360	104.6 ± 0.8	192.7 ± 2.3			

[a] Uncertainties are expressed as the expanded uncertainty (0.95 level of confidence, k = 2). [b] Calculated from Eq. (2) for two different temperatures (ϑ represents the mean temperature of the experiments or the temperature 298.15 K).

[c] Calculated using Eq. (3); uncertainties calculated through the RSS method. [d] σ_{r} is the relative standard deviation of the fit, defined as $\sigma_{\mathrm{r}} = \left[\sum_{i=1}^{n} (\ln p - \ln p_{\mathrm{calc}})_i^2 / (n-m)\right]^{1/2}$. [e] Calculated as $\Delta_{\mathrm{cr}}^{\mathrm{g}} C_{p,\mathrm{m}}^{\mathrm{o}}(\theta) = C_{p,\mathrm{m}}^{\mathrm{o}}(\mathrm{g}) - C_{p,\mathrm{m}}^{\mathrm{o}}(\mathrm{cr})$. [f] Mean temperature.

Table 5: Standard ($p^o = 10^5$ Pa) thermodynamic properties of sublimation of *N*,*N*-dimethyl-4-nitroaniline.

When the experimental determination of crystalline or liquid vapor pressures is performed over a wide temperature interval, (approximately 50 K), the fitting of equation 2 to (p,T) results may yield accurate values of $\Delta_{\mathrm{cd}}^{\mathrm{g}} C_{p,\mathrm{m}}^{\mathrm{o}}$. In this work, the temperature range of those determinations was not large enough (approximately 22 K), therefore the value of $\Delta_{\mathrm{cr}}^{\mathrm{g}} C_{p,\mathrm{m}}^{\mathrm{o}}$ could not be accurately derived. So, it was determined as $\Delta_{\mathrm{cr}}^{\mathrm{g}} C_{p,\mathrm{m}}^{\mathrm{o}} = C_{p,\mathrm{m}}^{\mathrm{o}}(\mathrm{g}) - C_{p,\mathrm{m}}^{\mathrm{o}}(\mathrm{cr})$, where $C_{p,\mathrm{m}}^{\mathrm{o}}(\mathrm{g})$ and $C_{p,\mathrm{m}}^{\mathrm{o}}(\mathrm{cr})$ are, respectively, the gas and crystalline isobaric molar heat capacities. The value of $C_{p,\mathrm{m}}^{\mathrm{o}}(\mathrm{g})$ determined at the temperature 298.15 K, $C_{p,\mathrm{m}}^{\mathrm{o}}(\mathrm{g}, 298.15\,\mathrm{K})$ / J·K⁻¹·mol⁻¹ = (186.6 ± 5.6), was derived from statistical thermodynamics, calculated by means of the Gaussian 09 software package (Frisch et al. 2010), using the vibrational frequencies from G3(MP2)//B3LYP calculations (scaled by a factor of (0.960 ± 0.022) (NIST 2013)).

The DSC results of the crystalline heat capacities, $C_{p,\mathrm{m}}^{\mathrm{o}}(\mathrm{cr})$, referred to above, were determined at different temperatures, enabling the fit to a second-order polynomial in temperature, represented by Equation (4), with a correlation coefficient of 0.999.

$$C_{p,\mathrm{m}}^{\mathrm{o}}(\mathrm{cr}) / \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}} = 241.3 - 0.6348\,(T/K) + 1.804x10^{-3}\,(T^2/\mathrm{K}) \tag{4}$$

At 298.15 K, the value $C^{\circ}_{p,\mathrm{m}}(\mathrm{cr})$ / J·K^{-1}·mol^{-1} = (212.4 ± 3.7) was derived, allowing to obtain the result $\Delta^{\mathrm{g}}_{\mathrm{cr}}C^{\circ}_{p,\mathrm{m}}$ / J·K^{-1}·mol^{-1} = (–25.8 ± 6.7), that was introduced in Equation (2).

Figure 1 shows the plot of the sublimation vapor pressures against reciprocal temperatures determined in this work for 4DMNA. Additionally, the figure includes a few sublimation results reported in the literature for this compound, which were also determined based on the dependence of vapor pressure on temperature.

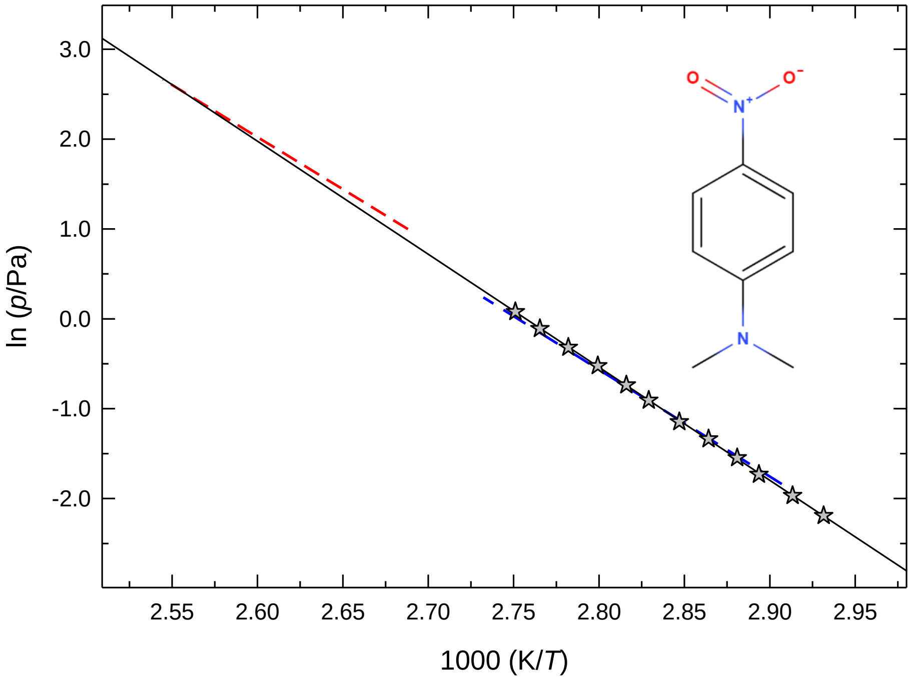

Figure 1: Graphical representation of vapor pressures against reciprocal temperature for *N*,*N*-dimethyl-4-nitroaniline. Star, effusion vapor pressures determined in this work. Red dashed line, crystalline vapor pressures from the reported equation ln(p/Pa) = (32.245 ± 0.050) – (11624 ± 220) (K/T) (Acree et al. 1994); Blue dashed line, crystalline vapor pressures from the reported equation log10(p/kPa) = 11.210 – 5163/(T/K) (Stephenson and Malanowski 1987).

Acree *et al*. (Acree et al. 1994) determined sublimation vapor pressures of *N*,*N*-dimethyl-4-nitroaniline, between 372 K and 393 K, using a Knudsen-type cell placed in a Calvet standard microcalorimeter, deriving the following vapor pressure equation (5).

$$\ln(p/\mathrm{Pa}) = (32.245 \pm 0.050) - (11624 \pm 220)\ (\mathrm{K}/T) \qquad (5)$$

The authors adjusted the value of the enthalpy of sublimation at the mean temperature of the experiments to 298.15 K (using $\Delta^{\mathrm{g}}_{\mathrm{cr}}C^{\circ}_{p,\mathrm{m}}$ = –50 J·K^{-1}·mol^{-1}) obtaining the value $\Delta^{\mathrm{g}}_{\mathrm{cr}}H^{\circ}_{\mathrm{m}}$ (298.15 K) = (101.3 ± 2.0) kJ·mol^{-1} (Acree et al. 1994). Taking into account the experimental result of $\Delta^{\mathrm{g}}_{\mathrm{cr}}C^{\circ}_{p,\mathrm{m}}$ (298.15 K) = (–25.8 ± 6.7) J·K^{-1}·mol^{-1} determined in this study, the value $\Delta^{\mathrm{g}}_{\mathrm{cr}}H^{\circ}_{\mathrm{m}}$ (298.15 K) = (98.8 ± 2.0) kJ·mol^{-1} was derived, that is 7.2 kJ·mol^{-1} smaller than the result determined in this work at the same temperature. Considering the limited experimental details provided in the refereed reference, it is challenging to speculate on the reasons for the observed differences.

However, it is noteworthy that the discrepancies seem to lie in the results of vapor pressures measured at temperatures below 384 K (see Figure 1). Beyond this temperature, the vapor pressures are similar to those determined in this work.

Stephenson and Malanowski (Stephenson and Malanowski 1987) also reported an equation for crystalline vapor pressures of the compound studied, collected from uncited literature sources. These authors reported Equation (6) that was derived from data determined between 344 K and 366 K.

$$\log_{10}(p/\text{kPa}) = 11.210 - 5163/(T/\text{K}) \qquad (6)$$

At the mean temperature of the experimental measurements, this equation yields the value $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}$(355 K) = (98.7 ± 1.7) kJ·mol^{-1}. Using the $\Delta_{\text{cr}}^{\text{g}}C_{p,\text{m}}^{\text{o}}$(298.15 K) value obtained in this work, that result was adjusted to 298.15 K, yielding $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}$(298.15 K) = (100.2 ± 1.7) kJ·mol^{-1}, that is 5.8 kJ·mol^{-1} smaller than the value determined by us. After converting Equation (6) to ln(p/Pa), the lines originated by the referred to above equations were represented in Figure 1 together with the mean effusion vapor pressure values measured in this work.

By means of a sublimation calorimetric system incorporating a Calvet microcalorimeter, Furukawa *et al* (Furukawa et al. 1984) determined the value $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}$(298.15 K) = (102.7 ± 1.1) kJ.mol^{-1} for 4DMNA, which is 3.3 kJ·mol^{-1} smaller than the one determined in this study.

Taking into account the second member of Equation (3), the volatility (related with $\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^{\text{o}}(T)$) of a compound increases with decreasing $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}(T)$ and increasing values of the product [$T\Delta_{\text{cr}}^{\text{g}}S_{\text{m}}^{\text{o}}(T)$]. The influence of the enthalpic and entropic factors for the values of $\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^{\text{o}}$ (298.15 K) of 4DMNA are clearly noted in Figure 2, indicating that the volatility is greatly conditioned by enthalpic reasons.

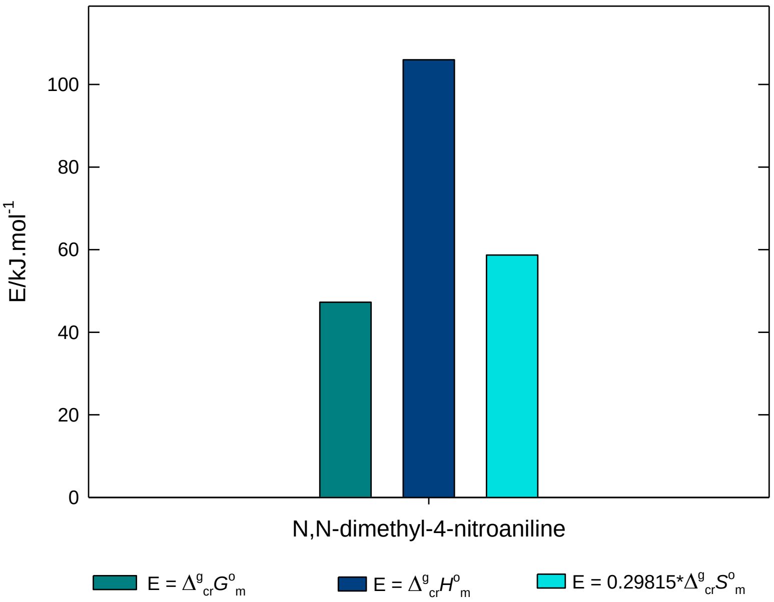

Figure 2: Relation between $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}$, $\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^{\text{o}}$ and $T\Delta_{\text{cr}}^{\text{g}}S_{\text{m}}^{\text{o}}$ of *N*,*N*-dimethyl-4-nitroaniline.

3. Conclusions

This research work presents an experimental thermodynamic study on the fusion and sublimation properties of the chromophore *N*,*N*-dimethyl-4-nitroaniline. The following are the key conclusions drawn from this study:

- The temperature and molar enthalpy of fusion of this compound, along with its isobaric crystalline heat capacities, were determined using differential scanning calorimetry. The obtained results for the fusion properties were as follows: T_{fus} = (435.3 ± 0.5) K and $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{\mathrm{o}}(T_{\mathrm{fus}})$ = (27.4 ± 0.2) kJ·mol^{-1}. The crystalline heat capacities were fitted with a second-order polynomial in temperature: $C_{p,\mathrm{m}}^{\mathrm{o}}(\mathrm{cr})$/J·K^{-1}·mol^{-1} = 241.3 - 0.6348 (T/K) + 1.804x10^{-3} (T^2/K), yielding the value $C_{p,\mathrm{m}}^{\mathrm{o}}(\mathrm{cr})$ = (212.4 ± 3.7) J·K^{-1}·mol^{-1} at 298.15 K.

- The sublimation vapor pressures of this compound were measured using a well-tested Knudsen mass-loss effusion technique, within the temperature range between 341.1 K and 363.5 K. From the (p,T) experimental results, the standard molar enthalpy, entropy, and Gibbs energy of sublimation were calculated for the compound under study. The determined result, $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(298.15\,\mathrm{K})$ = (106.0 ± 0.8) kJ·mol^{-1}, was compared with the few results reported in the literature. This value is, respectively, 7.2 kJ·mol^{-1}, 5.8 kJ·mol^{-1} and 3.3 kJ·mol^{-1} larger than the results determined in this work from the values reported in the literature by (Acree et al. 1994), (Stephenson and Malanowski 1987) and (Furukawa et al. 1984).

- Using statistical thermodynamics, the value of the gas phase heat capacity, at the temperature of 298.15 K, was determined as $C_{p,\mathrm{m}}^{\mathrm{o}}(\mathrm{g})$ = (186.6 ± 5.6) J·K^{-1}·mol^{-1}.

- Taking into consideration the well-established relation, $\Delta_{\mathrm{cr}}^{\mathrm{g}}G_{\mathrm{m}}^{\mathrm{o}}(\theta)=\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(\theta)-\theta\cdot\Delta_{\mathrm{cr}}^{\mathrm{g}}S_{\mathrm{m}}^{\mathrm{o}}(\theta)$, the enthalpic and entropic contributions to the volatility of the compound studied were evaluated. It was found that the enthalpic term significantly influenced the volatility of *N*,*N*-dimethyl-4-nitroaniline.

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References

Acree, William E., Sheryl A. Tucker, Gerald Pilcher, and Geraldine Toole. 1994. "Enthalpies of Combustion of 4-Dimethylamino-Nitrosobenzene and 4-Dimethylaminonitrobenzene." *The Journal of Chemical Thermodynamics* 26 (1): 85–90. https://doi.org/10.1006/jcht.1994.1023.

Almeida, Ana R. R. P., Bruno D. A. Pinheiro, Carlos F. R. A. C. Lima, Ana Filipa L. O. M. Santos, António C. S. Ferreira, Filipe A. Almeida Paz, and Manuel J. S. Monte. 2019. "Thermodynamic Properties of Moldy-Musty Contaminants of Wine." *Journal of Chemical & Engineering Data* 64 (11): 4741–53. https://doi.org/10.1021/acs.jced.9b00062.

Almeida, Ana R. R. P., M. Agostinha R. Matos, Manuel J. S. Monte, and Victor M. F. Morais. 2012. “Experimental and Computational Thermodynamic Study of Ortho-, Meta-, and Para-Methylbenzamide.” *The Journal of Chemical Thermodynamics* 47 (April): 81–89. https://doi.org/10.1016/j.jct.2011.09.024.

Almeida, Ana R. R. P., and Manuel J. S. Monte. 2013. “Crystalline and Liquid Vapour Pressures of the Four P-Monohalophenols: A Thermodynamic Study of Their Phase Transitions.” *The Journal of Chemical Thermodynamics* 65 (October): 150–58. https://doi.org/10.1016/j.jct.2013.05.047.

Almeida, Ana R. R. P., Juliana A. S. A. Oliveira, and Manuel J. S. Monte. 2015. “Thermodynamic Study of Nicotinamide, N-Methylnicotinamide and N,N-Dimethylnicotinamide: Vapour Pressures, Phase Diagrams, and Hydrogen Bonds.” *The Journal of Chemical Thermodynamics* 82 (March): 108–15. https://doi.org/10.1016/j.jct.2014.11.001.

Almeida, Ana R. R. P., Bruno D. A. Pinheiro, Ana I. M. C. Lobo Ferreira, and Manuel J. S. Monte. 2022. “Study on the Volatility of Four Benzaldehydes.” *Thermochimica Acta* 717 (November): 179357. https://doi.org/10.1016/j.tca.2022.179357.

Baboul, Anwar G., Larry A. Curtiss, Paul C. Redfern, and Krishnan Raghavachari. 1999. “Gaussian-3 Theory Using Density Functional Geometries and Zero-Point Energies.” *The Journal of Chemical Physics* 110 (16): 7650–57. https://doi.org/10.1063/1.478676.

Baptista, Rosa M. F., Bruna Silva, João Oliveira, Vahideh B. Isfahani, Bernardo Almeida, Mário R. Pereira, Nuno Cerca, et al. 2022. “High Piezoelectric Output Voltage from Blue Fluorescent N,N-Dimethyl-4-Nitroaniline Nano Crystals in Poly-L-Lactic Acid Electrospun Fibers.” *Materials* 15 (22): 7958. https://doi.org/10.3390/ma15227958.

Borbulevych, Oleg Ya, Ronald D. Clark, Angela Romero, Li Tan, Mikhail Yu Antipin, Vladimir N. Nesterov, Beatriz H. Cardelino, Craig E. Moore, Mohan Sanghadasa, and Tatiana V. Timofeeva. 2002. “Experimental and Theoretical Study of the Structure of N,N-Dimethyl-4-Nitroaniline Derivatives as Model Compounds for Non-Linear Optical Organic Materials.” *Journal of Molecular Structure* 604 (1): 73–86. https://doi.org/10.1016/S0022-2860(01)00642-1.

Campbell, Tod W. 1949. “A Convenient Synthesis of N,N-Dimethyl- *p* -Nitroaniline and N,N-Dimethyl- *o* -Nitroaniline.” *Journal of the American Chemical Society* 71 (2): 740–740. https://doi.org/10.1021/ja01170a502.

Chang, S. S., and A. B. Bestul. 1972. “Heat Capacity and Thermodynamic Properties of *o* -Terphenyl Crystal, Glass, and Liquid.” *The Journal of Chemical Physics* 56 (1): 503–16. https://doi.org/10.1063/1.1676895.

Clarke, E. C. W., and D. N. Glew. 1966. “Evaluation of Thermodynamic Functions from Equilibrium Constants.” *Transactions of the Faraday Society* 62: 539. https://doi.org/10.1039/tf9666200539.

Costela, A, I García-Moreno, O García, and R Sastre. 2001. “Laser-Assisted Photochemistry of N,N-Dimethyl-4-Nitroaniline Initiator of Polymerization.” *Chemical Physics Letters* 347 (1–3): 115–20. https://doi.org/10.1016/S0009-2614(01)01034-X.

Curtiss, Larry A., Krishnan Raghavachari, Paul C. Redfern, Vitaly Rassolov, and John A. Pople. 1998. “Gaussian-3 (G3) Theory for Molecules Containing First and Second-Row Atoms.” *The Journal of Chemical Physics* 109 (18): 7764–76. https://doi.org/10.1063/1.477422.

Frisch, M. J., G. W. Trucks, H. B. Schlegel, G. E. M. A. Robb, Scuseria, and M. A. Robb. 2010. “Gaussian 03, Revision.”

Furukawa, G. T., R. E. McCoskey, and G. J. King. 1951. “Calorimetric Properties of Benzoic Acid from 0 to 410 K.” *Journal of Research of the National Bureau of Standards* 47 (4): 256–61.

Furukawa, Junichi, Shigeo Murata, Minoru Sakiyama, and Syûzô Seki. 1984. “Thermochemical Studies on 3- and 4-Nitroanilines and Their *N* , *N* -Dimethyl Derivatives.” *Bulletin of the Chemical Society of Japan* 57 (11): 3058–61. https://doi.org/10.1246/bcsj.57.3058.

Gatta, Giuseppe Della, Michael J. Richardson, Stefan M. Sarge, and Svein Stølen. 2006. “Standards, Calibration, and Guidelines in Microcalorimetry. Part 2. Calibration Standards for Differential Scanning Calorimetry* (IUPAC Technical Report).” *Pure and Applied Chemistry* 78 (7): 1455–76. https://doi.org/10.1351/pac200678071455.

Mohr, Peter J., David B. Newell, and Barry N. Taylor. 2016. “CODATA Recommended Values of the Fundamental Physical Constants: 2014.” *Reviews of Modern Physics* 88 (3): 035009. https://doi.org/10.1103/RevModPhys.88.035009.

Monte, Manuel J. S., Ana R. R. P. Almeida, and Rafael Notario. 2018. “Volatility and Chemical Stability of Chromium, Molybdenum, and Tungsten Hexacarbonyls.” *Journal of Thermal Analysis and Calorimetry* 132 (2): 1201–11. https://doi.org/10.1007/s10973-018-7033-1.

Murata, S., M. Sakiyama, and S. Seki. 1985. “Sublimation Calorimetric Studies Using a Calvet Microcalorimeter.” *Thermochimica Acta* 88 (1): 121–26. https://doi.org/10.1016/0040-6031(85)85419-8.

Nakano, Hiroshi. 2015. “Solvent Electronic Polarization Effects on a Charge Transfer Excitation Studied by the Mean-Field QM/MM Method.” In , 090057. https://doi.org/10.1063/1.4938865.

Netzsch. 2022. NETZSCH Analyzing & Testing DSC 204 F1 Phoenix. Calibration set. 2022, Selb, Germany. Accessed 19 April, 2023. https://analyzingtesting.netzsch.com/Resources/Persistent/3/f/6/2/3f62fce9e4fd19c3cb5d75f1514a90ef444f9c23/DSC_204_F1_Phoenix_en_web.pdf

NIST. 2013. NIST Computational Chemistry Comparison and Benchmark Database. 2013. NIST Standard Reference Database Number 101, Release 16a; Johnson, R.D., III, Ed.; NIST Chemistry Webbook. SRD 69. Accessed 10 March, 2023: http://cccbdb.nist.gov/vibscalejust.asp

Perez-Prado, Maria T., and Michael E. Kassner. 2015. “Superplasticity.” In *Fundamentals of Creep in Metals and Alloys*, 139–57. Elsevier. https://doi.org/10.1016/B978-0-08-099427-7.00006-2.

Ramezannejad, A., W. Xu, and M. Qian. 2018. “Ni-Free Superelastic Titanium Alloys for Medical and Dental Applications.” In *Titanium in Medical and Dental Applications*, 591–611. Elsevier. https://doi.org/10.1016/B978-0-12-812456-7.00028-7.

Ribeiro da Silva, Manuel A. V., Manuel J. S. Monte, Ana I. M. C. Lobo Ferreira, Juliana A. S. A. Oliveira, and Álvaro Cimas. 2010. “A Combined Experimental and Computational Thermodynamic Study of Difluoronitrobenzene Isomers.” *The Journal of Physical Chemistry B* 114 (40): 12914–25. https://doi.org/10.1021/jp1058885.

Ribeiro da Silva, Manuel A. V., Manuel J. S. Monte, and Luís M. N. B. F. Santos. 2006. “The Design, Construction, and Testing of a New Knudsen Effusion Apparatus.” *The Journal of Chemical Thermodynamics* 38 (6): 778–87. https://doi.org/10.1016/j.jct.2005.08.013.

Roux, María Victoria, Manuel Temprado, James S. Chickos, and Yatsuhisa Nagano. 2008. “Critically Evaluated Thermochemical Properties of Polycyclic Aromatic Hydrocarbons.”

Journal of Physical and Chemical Reference Data 37 (4): 1855–1996. https://doi.org/10.1063/1.2955570.

Sabbah, Raphael., An Xu-wu, James. S. Chickos, M. L. Planas Leitão, María. V. Roux, and Luis A. Torres. 1999. “Reference Materials for Calorimetry and Differential Thermal Analysis.” *Thermochimica Acta* 331 (2): 93–204. https://doi.org/10.1016/S0040-6031(99)00009-X.

Sabbah, Raphael., and L. E. Watik. 1992. “New Reference Materials for the Calibration (Temperature and Energy) of Differential Thermal Analysers and Scanning Calorimeters.” *Journal of Thermal Analysis* 38 (4): 855–63.

Stephenson, Richard M., and Stanislaw Malanowski. 1987. *Handbook of the Thermodynamics of Organic Compounds*. Dordrecht: Springer Netherlands. https://doi.org/10.1007/978-94-009-3173-2.

Zhang, Chao-Zhi, Hui Cao, and Zhao-Bing Guo. 2012. “Theoretical Study of Effect of the Number of N,N-Dimethyl-4-Nitroaniline Units in Novel ‘Parallel Connection’ Chromophores on Its Nonlinear Optical Properties.” *ISRN Physical Chemistry* 2012 (December): 1–8. https://doi.org/10.5402/2012/262563.