



Enthalpies of combustion, vapour pressures, and enthalpies of sublimation of the 1,5- and 1,8-diaminonaphthalenes

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ABSTRACT

The standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation, in the crystalline state, of 1,5-diaminonaphthalene and 1,8-diaminonaphthalene were derived from the standard molar energies of combustion, in oxygen, at $T = 298.15$ K, measured by static-bomb combustion calorimetry. The Knudsen mass-loss effusion technique was used to measure the dependence of the vapour pressure of the solid isomers of diaminonaphthalene with the temperature, from which the standard molar enthalpies of sublimation were derived using the Clausius–Clapeyron equation.

	$-\Delta_c U_m^\circ(\text{cr})/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_f H_m^\circ(\text{cr})/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_{\text{cr}}^g H_m^\circ/(\text{kJ} \cdot \text{mol}^{-1})$
1,5-Diaminonaphthalene	5402.7 ± 2.2	42.1 ± 2.6	122.5 ± 0.9
1,8-Diaminonaphthalene	5425.9 ± 2.3	65.4 ± 2.6	99.0 ± 0.7

Combining these two experimental values, the gas-phase standard molar enthalpies of formation, at $T = 298.15$ K, were derived and compared with those estimated using two different empirical methods of $\Delta_f H_m^\circ(\text{g})$ estimation: the Cox scheme and the Benson's Group Method.

Moreover, the standard ($p^\circ = 0.1$ MPa) molar entropies and Gibbs energies of sublimation, at $T = 298.15$ K, were derived for the two diaminonaphthalene isomers.

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1. Introduction

For over a decade, we have been focusing deep attention on the thermochemistry of aromatic compounds, where some polycyclic aromatic hydrocarbons are included, being this paper a contribution to the thermochemical investigation of naphthalene derivatives, carried out on the Molecular Energetics Research Group of the University of Porto, following the studies of hydroxy- and dihydroxynaphthalenes [1], bromonaphthalenes [2], and nitro-naphthalenes [3].

This work deals with the thermochemical study of the 1,5-diaminonaphthalene and 1,8-diaminonaphthalene (figure 1), under the general aim of studying the influence of the polar and steric ef-

fects of the substituents on the thermodynamic stability of the molecules.

Aromatic diamines are valuable building units for the design of interesting ligands, allowing the preparation of a wide array of Schiff bases, which are used in coordination chemistry [4–6]. The diaminonaphthalene is widely used in the preparation of polymers and conducting polymers due to their application in the field of organic batteries, sensors, electronic displays, and semiconductor devices [7–11]. At the beginning of the 20th century more than hundreds of naphthalene derivatives had been prepared as components for azo dyes. Although, 1,5-aminonaphthalene has only limited use as a dye intermediate, being largely used as intermediate in the manufacture of naphthalene-1,5-diisocyanate, which is employed for specialty polyurethane polymers. This diaminonaphthalene isomer is considered by the International Agency for Research on Cancer (IARC) as a species having limited carcinogenicity in animals [12], and the human contact with this compound results in

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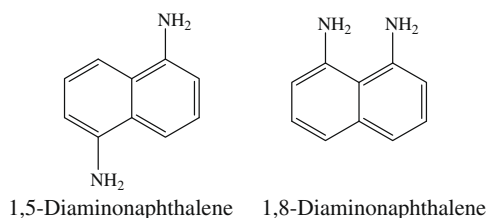


FIGURE 1. Structural formula of diaminonaphthalene isomers.

occupational exposure causing irritation and disorders in the airway [13].

The 1,8-diaminonaphthalene received special attention due to its unique properties: as polymer, one of the most remarkable characteristics of poly(1,8-diaminonaphthalene) is its ability to extract and form complexes with heavy metal cations (for example Ag^+ , Cu^{2+} and Hg^{2+}), enabling a number practical applications, such as heavy metal sensors [14]; and as proton spongers [15], which is related with the extraordinarily high basicity of these compounds, in particular of the 1,8-bis(dimethylamino)naphthalene, $\text{p}K_{\text{a}} = 12.1$. This characteristic seems to be due to spatial interaction of the basic centers, which are in close proximity.

For these two isomers, there is available in the literature [16] thermochemical data concerning the vapour pressures, enthalpies of sublimation, $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}$, enthalpies of vaporization, $\Delta_{\text{v}}^{\text{g}}H_{\text{m}}^{\circ}$, and enthalpies of fusion, $\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\circ}$, at the reference temperature 298.15 K. In that work, carried out by Verevkin *et al.* [16], the vapour pressures of the two diaminonaphthalene isomers have been determined by the transpiration method. The enthalpy of fusion of 1,8-diaminonaphthalene was measured by DSC and, for 1,5-diaminonaphthalene, it was calculated using the modified Walden's rule [17]. The values of the enthalpies of sublimation/vaporization and enthalpies of fusion, given by Verevkin *et al.* [16], were $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ} = (120.16 \pm 0.65) \text{ kJ} \cdot \text{mol}^{-1}$, and $\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\circ} = 14.6 \text{ kJ} \cdot \text{mol}^{-1}$, for the 1,5-diaminonaphthalene and $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ} = (94.08 \pm 0.37) \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta_{\text{v}}^{\text{g}}H_{\text{m}}^{\circ} = (79.57 \pm 0.25) \text{ kJ} \cdot \text{mol}^{-1}$, and $\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\circ} = 13.5 \text{ kJ} \cdot \text{mol}^{-1}$, for 1,8-diaminonaphthalene isomer.

The crystalline structure of the 1,5-diaminonaphthalene has been recently solved by Bernès *et al.* [18]. This isomer has unit cell with a monoclinic, $P2_1/c$ crystal system and a space group $P2_1/c$, and crystallizes with one and a half molecules in the asymmetric unit, one lying on a general position and the other on an inversion centre. The dihedral angle between these two molecules is 73.30° . The molecular structure of 1,8-diaminonaphthalene has also been solved by X-ray crystallography by Llamas-Saiz and co-workers [19], which was also compared with the results of a theoretical analysis at the AM1 level. This molecule has a unit cell with an orthorhombic crystal system and a space group $P_{na}2_1$.

The present study provides results on the purification, standard molar energy of combustion, standard molar enthalpy of sublimation, and standard molar enthalpy of formation in both crystalline and gaseous state, $T = 298.15 \text{ K}$, for the two title compounds. The standard ($p^\circ = 0.1 \text{ MPa}$) molar enthalpies of formation, in the crystalline state, of the two isomers, at $T = 298.15 \text{ K}$, were derived from the standard massic energies of combustion, measured by static-bomb calorimetry. The Knudsen mass-loss effusion technique was used to measure the vapour pressures as a function of temperature of the two crystalline compounds. From the temperature dependence of the vapour pressure, and by application of the Clausius–Clapeyron equation, the standard molar enthalpies of sublimation, at the mean temperature of the experimental temperature range, were derived. Standard molar enthalpies, entropies, and Gibbs energies of sublimation, at the temperature of 298.15 K, were calculated using estimated values for the heat capacity differences between the gas and the crystal phases of each compound.

The values of the standard molar enthalpy of formation, in the crystalline phase, and of the standard molar enthalpy of sublimation were combined to derive the standard molar enthalpies of formation, in the gaseous phase, at $T = 298.15 \text{ K}$, of the two compounds. The same parameter was estimated by the Cox scheme [20] and by the Benson group additivity method [21] for the two diaminonaphthalene isomers.

2. Experimental

2.1. Materials and purity control

Samples of 1,5-diaminonaphthalene, [CAS 2243-62-1] and 1,8-diaminonaphthalene, [CAS 479-27-6] were supplied by Aldrich Chemical Co. with an assessed mass fraction minimum purity of 0.97 and 0.99, respectively, and purified in this laboratory. The purification of the 1,5-diaminonaphthalene was carried out by vacuum sublimation at 0.1 Pa background pressure and $T = 408 \text{ K}$, followed by recrystallization from aqueous ethanol. The 1,8-diaminonaphthalene was purified firstly by sublimation at 0.1 Pa background pressure and $T = 323 \text{ K}$, and then was recrystallized from methanol. The samples of both isomers were dried in vacuum till free from methanol/ethanol. The crystals of 1,8-diaminonaphthalene decompose and lose the crystalline character within a few days, becoming brown on standing. Therefore, during the experimental work, the samples of both isomers were stored in vacuum and kept away from light.

The final purity of each isomer was checked by gas liquid chromatography, performed on an Agilent 4890D gas chromatograph equipped with an HP-5 column, cross-linked, 5% diphenyl and 95% dimethylpolysiloxane ($15 \text{ m} \times 0.530 \text{ mm i.d.} \cdot 1.5 \mu\text{m}$ film thickness), and with nitrogen as carrier gas. The temperature of the injector was set at 473 K and the oven temperature was programmed as follows: $T = 323 \text{ K}$ (60 s), ramp at $0.167 \text{ K} \cdot \text{s}^{-1}$, 473 K (300 s). No impurities greater than 10^{-3} in mass fraction could be detected in the samples of both isomers used for the static-bomb combustion calorimetry and for the Knudsen effusion technique.

These purities were also confirmed by the mass of carbon dioxide recovered in the combustion experiments to that calculated from the mass of the sample; the averages, together with the standard deviation of the mean, were: 1,5-diaminonaphthalene (1.0002 ± 0.0003) and 1,8-diaminonaphthalene (1.0000 ± 0.0004).

The relative atomic masses used in the calculation of all molar quantities throughout this paper were those recommended by the IUPAC Commission in 2005 [22]; using those values, the molar mass for the 1,5- and 1,8-diaminonaphthalenes is $158.1998 \text{ g} \cdot \text{mol}^{-1}$.

2.2. Combustion calorimetry measurements

The combustion experiments were performed with a static-bomb calorimeter, with a twin valve combustion bomb Type 1105, Parr Instrument Company, made of stainless steel, with an internal volume of 0.340 dm^3 ; the apparatus and technique have been previously described [23,24]. The energy equivalent, $\varepsilon(\text{calor})$, of the calorimeter was determined from the combustion of benzoic acid (NIST Standard Reference Material 39j), having a massic energy of combustion under bomb conditions of $-(26434 \pm 3) \text{ J} \cdot \text{g}^{-1}$ [25]. The calibration results were corrected to give the $\varepsilon(\text{calor})$ corresponding to the average mass of water added to the calorimeter: 3119.6 g . From eight calibration experiments, performed according to the procedure suggest by Coops *et al.* [26], $\varepsilon(\text{calor}) = (15906.6 \pm 1.9) \text{ J} \cdot \text{K}^{-1}$, where the quoted uncertainty refers to the standard deviation of the mean.

For all experiments, samples in pellet form were ignited at $T = (298.150 \pm 0.001) \text{ K}$ in oxygen at a pressure of 3.04 MPa, with

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