



# Experimental and computational thermodynamics of pyrene and 1-pyrenecarboxaldehyde and their photophysical properties



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## ABSTRACT

A combined experimental and computational study was performed to evaluate the energetics, stability and volatility of pyrene and 1-pyrenecarboxaldehyde. The standard ( $p^\circ = 0.1$  MPa) molar enthalpy of combustion,  $\Delta_c H_m^\circ$ , of 1-pyrenecarboxaldehyde was measured by static bomb combustion calorimetry, from which its standard ( $p^\circ = 0.1$  MPa) molar enthalpy of formation, in the crystalline phase, at  $T = 298.15$  K, was derived. The vapour pressures of the two compounds were measured at different temperatures using the Knudsen mass-loss effusion method enabling the determination of molar standard enthalpies and entropies of sublimation at the mean temperatures of the experiments and at 298.15 K, using estimated values of  $\Delta_{cr}^g C_{p,m}^\circ$  for the temperature adjustments. The temperature and the molar enthalpy of fusion of both compounds were determined using differential scanning calorimetry. From fluorescence spectroscopy measurements, their photophysical properties, in solution and in the solid state, were determined. The experimental thermodynamic and luminescence results were compared with values available in the literature.

Additionally, standard *ab initio* molecular calculations, at the G3(MP2)//B3LYP level, were performed and the standard enthalpies of formation of these two compounds were estimated. A very good agreement between the calculated and the experimental data was obtained. Furthermore, the results were interpreted in terms of enthalpic increments. The gas-phase molar heat capacities and absolute entropies of the two compounds studied were also calculated.

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## 1. Introduction

The discovery and test of new organic semi-conductor materials with high electroluminescence efficiency and adequate chemical and thermal stabilities to be used either in lighting or in electronic devices, such as organic light emitting diodes (OLEDs) and organic photovoltaic solar cells (OPVs), is one of the most important aspects in materials science. Among these fluorescent materials are some polycyclic aromatic hydrocarbons (PAHs) being most of these considered carcinogenic or mutagenic products [1]. Vapour pressure is one of the key properties that control their fate in the environment. Thus, its knowledge is very useful to complement the information needed to predict PAHs behaviour in the environment [2]. Generally, PAHs have low vapour pressures and tend to accumulate in living beings, soils, sediments and are adsorbed on particulate matter [3]. The prediction of the behaviour and reaction kinetics of these substances requires an accurate description of

their thermochemical and thermophysical properties which are also useful in designing processes to generate new ones and for predicting their potential for application in electronic devices. So, in this work, we have focused our attention in the determination of relevant thermodynamic parameters and characterisation of the luminescence properties of two PAHs – pyrene and 1-pyrenecarboxaldehyde.

Static bomb combustion calorimetry and mass-loss Knudsen effusion experiments were performed aiming, respectively, the determination of the enthalpy of formation, in the crystalline phase, and the standard molar enthalpy, entropy and Gibbs energy of sublimation of the 1-pyrenecarboxaldehyde. The sublimation properties of pyrene were also determined from Knudsen effusion experiments, but no combustion experiments were done in the present study because the literature result reported by Smith *et al.* [4] seems reliable.

The thermodynamic properties related to fusion and to eventual transitions between crystalline phases were determined for both compounds using differential scanning calorimetry. The thermodynamic stability of the compounds in both crystalline and gaseous

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phases was evaluated by the determination of the standard Gibbs energies of formation. Finally, the G3(MP2)//B3LYP approach allowed the estimation of the gas-phase standard molar enthalpies of formation of both compounds, which were compared with the experimental values.

The photophysical properties concerning the absorption and the emission processes, as well as the quantum yield of the compounds under study, in solution and in the solid phase, were determined by UV/vis and fluorescence spectroscopy. Pyrene and its derivatives have been studied intensively as organic chromophores [5,6], sensors [7,8], light emitting materials in OLEDs [9–12], organic field effect transistors (OFETs) [12,13] and organic photovoltaic devices (OPVs) [12]. Synthetic pyrene-appended systems are used as sensors for ATP [14], heparin [15], nucleotides [16,17], transition metal ions [18] and as probes to study protein conformation, conformational changes, protein folding and unfolding, protein-protein, protein-lipid, and protein-membrane interactions [19]. They also find application as building blocks for preparation of luminescent polymers [20]. The conformational changes induced upon the binding of the target analyte to the pyrene-appended complexes are monitored using the pyrene luminescence emission, due to the fluorescent properties changes between the complexes and the isolated pyrene units. Pyrene and 1-pyrenecarboxaldehyde find application as fluorescence probes [21,22], useful in biophysical studies of multimolecular aggregates. Moreover, 1-pyrenecarboxaldehyde has been incorporated in Langmuir–Blodgett films, with potential application in sensors and optoelectronic devices [23].

## 2. Experimental

### 2.1. Compounds and purity control

The purification details and the provenance of the samples of pyrene [CAS 129-00-0] and 1-pyrenecarboxaldehyde [CAS 3029-19-4], studied in this work, are summarised in table 1. The final purity of 1-pyrenecarboxaldehyde was also assessed by the percentage of carbon dioxide recovered during the combustion experiments; the average ratio of the mass of carbon dioxide recovered to those calculated from the mass of samples used in each experiment, together with the uncertainty (expanded uncertainty of the mean, 0.95 level of confidence,  $k=2$ ) was  $(1.0001 \pm 0.0004)$ . The value of the specific density used for 1-pyrenecarboxaldehyde, was  $\rho = 1.194 \text{ g} \cdot \text{cm}^{-3}$  [24] and the relative atomic masses used for the elements were the ones recommended by the IUPAC Commission in 2011 [25].

### 2.2. Differential scanning calorimetry

The temperature and the enthalpy of fusion of pyrene and 1-pyrenecarboxaldehyde were determined using a PerkinElmer Diamond Pyris 1 differential scanning calorimeter. The power and temperature scales of the calorimeter were calibrated by measuring the melting temperature of the following reference materials: benzoic acid, triphenylene, naphthalene, anthracene, 1,3,5-triphenylbenzene, diphenylacetic acid, perylene, *o*-terphenyl

and 4-methoxybenzoic acid. For each compound, five independent runs were performed. Fresh samples, sealed in aluminium crucibles, were scanned from  $T = 298 \text{ K}$  to about 20 K above the temperature of fusion, at a heating rate of  $3.3 \cdot 10^{-2} \text{ K} \cdot \text{s}^{-1}$ , under a continuous nitrogen flux of  $0.8 \text{ mL} \cdot \text{s}^{-1}$ . The recorded thermograms were used to compute the onset temperatures of fusion,  $T_{\text{fus}}$ , and the enthalpies of fusion,  $\Delta_{\text{cr}}^{\text{l}} H_{\text{m}}^{\circ}(T_{\text{fus}})$ , of the two compounds as well as the temperature and enthalpy of the observed crystal-crystal phase transition of 1-pyrenecarboxaldehyde.

### 2.3. Combustion calorimetry

The combustion experiments on 1-pyrenecarboxaldehyde were performed in an isoperibol static bomb calorimetric system, equipped with a stainless steel twin valve bomb (Parr 1108 model), with an internal volume of  $0.342 \text{ dm}^3$ . The descriptions of the apparatus, as well as the operating technique have been previously reported [26,27]. The energy equivalent of the calorimeter was determined by the combustion of benzoic acid NIST Standard Reference Material, sample 39j, (under the bomb conditions,  $\Delta_{\text{cr}} u = -(26434 \pm 3) \text{ J} \cdot \text{g}^{-1}$ ) [28], according to Coops *et al.* [29]; the value obtained was  $\varepsilon(\text{calor}) = (16002.6 \pm 1.7) \text{ J} \cdot \text{K}^{-1}$ , as a mean of six calibration experiments, for an average mass of water added to the calorimeter of  $3119.6 \text{ g}$  (the quoted uncertainty refers the standard deviation of the mean). Pellets of crystalline 1-pyrenecarboxaldehyde were ignited in oxygen ( $x_{\text{O}_2} \geq 0.99995$ ), at  $T = (298.150 \pm 0.001) \text{ K}$ , under a pressure of  $3.04 \text{ MPa}$  (the bomb was previously flushed to remove air), with  $1.00 \text{ cm}^3$  of deionized water introduced into the bomb. The uncertainty of the measured temperatures is estimated to be  $u(T/\text{K}) = \pm 0.0001$ . Details about calorimetric temperature measurements, electrical energy for ignition, cotton thread fuse and the energetic effect for the amount of nitric acid produced in the combustion are described in previous works [30,31]. The quantity of compound,  $m(\text{cpd})$ , burnt in each experiment and on which the energy of combustion was based, was determined from the mass of  $\text{CO}_2$  produced, taking into account that formed from the combustion of the cotton thread fuse. The value for the pressure coefficient of specific energy,  $(\partial u/\partial p)_T$ , at  $T = 298.15 \text{ K}$ , was assumed to be  $-0.2 \text{ J} \cdot \text{g}^{-1} \cdot \text{MPa}^{-1}$ , a typical value for most organic compounds [32]. Corrections to the standard state,  $\Delta U_{\Sigma}$ , used for the calculation of the standard massic energy of combustion,  $\Delta_{\text{cr}} u^{\circ}$ , were made following the procedure proposed by Hubbard *et al.* [33].

### 2.4. Knudsen effusion technique

The vapour pressures of pyrene and 1-pyrenecarboxaldehyde were measured at different temperatures using the mass-loss Knudsen effusion method, which allowed the determination of their enthalpies of sublimation. The Knudsen apparatus used, fully described and tested before [34,35], enables the simultaneous operation of nine aluminium effusion cells, which are placed in cylindrical holes inside three aluminium blocks, each one with three cells with different areas of the effusion orifices, and maintained at a constant temperature, different from the other two blocks. The effusion orifices were made in platinum

**TABLE 1**  
Purification details of the compounds studied.

Chemical name	CAS	Supplier	Initial purity <sup>a</sup>	Purification method	Final mass fraction purity	Analysis method <sup>b</sup>
Pyrene (cr)	129-00-0	Sigma-Aldrich	0.989	Sublimation	0.9989	GC
1-Pyrenecarboxaldehyde (cr)	3029-19-4	Sigma-Aldrich	0.993	Sublimation	0.9991	GC

<sup>a</sup> According to the respective certificate of analysis.

<sup>b</sup> Gas-liquid chromatography (FID).

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