



## Study on the volatility of halogenated fluorenes



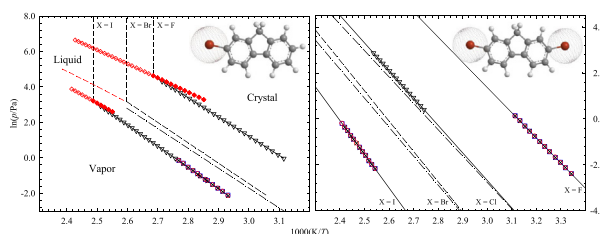
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### HIGHLIGHTS

- Phase transition properties of halo-fluorenes were determined.
- Vapor pressures of the compounds were measured at different temperatures.
- Vapor pressures and enthalpies of sublimation and vaporization were also estimated.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 15 March 2016  
 Received in revised form  
 4 May 2016  
 Accepted 6 May 2016  
 Available online 17 May 2016

Handling Editor: I. Cousins

#### Keywords:

Halogenated fluorenes  
 Vapor pressure  
 Sublimation  
 Vaporization  
 Fusion  
 Estimations

### ABSTRACT

This work reports the experimental determination of relevant thermophysical properties of five halogenated fluorenes. The vapor pressures of the compounds studied were measured at different temperatures using two different experimental techniques. The static method was used for studying 2-fluorofluorene (liquid and crystal vapor pressures between 321.04 K and 411.88 K), 2-iodofluorene (liquid and crystal vapor pressures between 362.63 K and 413.86 K), and 2,7-dichlorofluorene (crystal vapor pressures between 364.64 K and 394.22 K). The Knudsen effusion method was employed to determine the vapor pressures of 2,7-difluorofluorene (crystal vapor pressures between 299.17 K and 321.19 K), 2,7-diiodofluorene (crystal vapor pressures between 393.19 K and 415.14 K), and (again) 2-iodofluorene (crystal vapor pressures between 341.16 K and 361.12 K). The temperatures and the molar enthalpies of fusion of the five compounds were determined using differential scanning calorimetry. The application to halogenated fluorenes of recently developed methods for predicting vapor pressures and enthalpies of sublimation and vaporization of substituted benzenes is also discussed.

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### 1. Introduction

A simple look at a list of common pollutants will show a great number of halogenated polycyclic aromatic hydrocarbons (halo-PAHs) (Fu et al., 1999; Sun et al., 2013), such as biphenyls, naphthalenes, phenanthrenes, pyrenes, etc, especially those containing chlorine and bromine. Polycyclic aromatic hydrocarbons are one of

the main classes of persistent and bioaccumulative environmental pollutants which result mainly from incomplete combustion of fuels and organic matter. Since PAHs are generally formed from the combustion of organic matter, they are usually found in a considerable amount in municipal incinerator fly ash (Tausch and Stehlik, 1985; Oehme et al., 1987; Sovocool et al., 1988; Horii et al., 2008). Halogen substitution can occur at the most reactive position of a PAH and halo-PAHs are easily formed from the reaction of the PAHs with various wastes upon incineration at high temperatures (Sovocool et al., 1988). Halo-PAHs are also found in urban air

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(Haglund et al., 1987; Nilsson and Oestman, 1993; Ohura et al., 2005), coal combustion (Eklund and Strömberg, 1983), soil (Krauss and Wilcke, 2003), snow (Haglund et al., 1987), automobile exhausts (Haglund et al., 1987), industrial waste (Koistinen et al., 1994a,b; Ma et al., 2009) and even in tap water (Shiraishi et al., 1985). They are often resistant to biological degradation and are not efficiently removed by conventional physicochemical methods (Hinchee et al., 1994).

From all the known carcinogenics, PAHs have been some of the most studied (Gelboin and Ts'o, 1978; White, 1986; Harvey, 1991; Luch, 2005). They are known to induce hazardous genotoxic effects and some have been proved to be carcinogenic and potentially tumorigenic. PAHs in general are not direct-acting mutagens and require metabolic activation to exert mutagenicity. Some halo-PAHs, however, exhibit direct-acting mutagenicity and their potential action will depend on the location of the halogen substituent (Fu et al., 1999).

The relative abundance and fate of PAHs in atmospheric air, water vapor and particulate matter is to a large extent conditioned by their volatility and molecular weight (Ravindra et al., 2008). Once emitted to the atmosphere, heavier PAHs tend to adsorb to particulate matter, while lighter PAHs tend to remain gaseous.

The thermodynamic properties of PAHs have been extensively studied in the last decades (Roux et al., 2008), however there is a distinct lack of data on halogenated PAHs namely on halogenated fluorenes. For the prediction of the behavior of these pollutants in the environment, accurate data on vapor pressures and enthalpies of sublimation and vaporization are needed to derive their volatility, solubility in water, distribution coefficients, etc (Delle Site, 1997).

In this work we present a thorough study on the volatility of some mono and dihalogenated fluorenes, complemented with recent data present in the literature (Oliveira et al., 2015). Recently published estimation methods for substituted benzenes (Monte and Almeida, 2013; Monte et al., 2015) have been found appropriate in estimating the volatility properties of the compounds studied and were also employed for predicting the volatility properties of other halogenated fluorenes.

## 2. Experimental

### 2.1. Compounds and purity control

The monohalogenated fluorene derivatives studied in this work – 2-fluorofluorene (CAS 343-43-1) and 2-iodofluorene (CAS 2523-42-4) – were commercially acquired, while the dihalogenated fluorene derivatives – 2,7-difluorofluorene (CAS 2195-50-8), 2,7-dichlorofluorene (CAS 7012-16-0) and 2,7-diiodofluorene (CAS 16218-28-3) – were synthesized according to procedures published in the literature, with minor modifications (York Jr., 1984, Perumattam et al., 1994 and Anémian et al., 2003, respectively).

**Table 1**  
Source, purification and analysis details of the studied compounds.

Chemical name	Source	Minimal initial purity	Purification method	Final mass fraction purity <sup>a</sup>
2-Fluorofluorene	TCI Europe	0.998 <sup>b</sup>	Sublimation	0.9999
2-Iodofluorene	Aldrich	0.990 <sup>b</sup>	Sublimation	0.9963
2,7-Difluorofluorene	This work	0.891 <sup>c</sup>	Sublimation	0.9992
2,7-Dichlorofluorene	This work	0.976 <sup>c</sup>	Recrystallization and sublimation	0.9994
2,7-Diiodofluorene	This work	0.979 <sup>c</sup>	Recrystallization and sublimation	0.9969

<sup>a</sup> Determined in the present work using GC.

<sup>b</sup> Values refers to GC analysis, as stated in the certificates of analysis of the manufacturer.

<sup>c</sup> Purity by GC after synthesis.

Along this framework, we also attempted to synthesize 2-chlorofluorene following different procedures described in the literature (Kodomari et al., 1988; Muathen, 1996; Hwang et al., 2009). Its purification, however, was not successful because it couldn't be separated efficiently from 2,7-dichlorofluorene formed as a by-product of the synthesis reactions. The thermodynamic properties of this compound were not measured but only estimated.

The synthesized compounds were identified by NMR and mass spectrometry. The <sup>1</sup>H NMR and <sup>13</sup>C NMR data were acquired, at room temperature, on a Bruker AMX 400 spectrometer operating at 400.15 and 101.0 MHz, respectively, and electron impact mass spectra (EI-MS) were measured on a VG AutoSpec instrument.

All compounds, synthesized or acquired, were further purified by sublimation under reduced pressure and the purity control of the samples was evaluated by gas chromatography (GC), performed on an Agilent 4890D Gas Chromatograph, equipped with an HP-5 column (0.05 diphenyl and 0.95 dimethylpolysiloxane by mole fraction) and a flame ionization detector, using dimethylformamide as solvent and nitrogen as carrier gas. The purity details of all compounds are summarized in Table 1. The details of the synthetic procedures used to obtain the fluorene derivatives referred to above as well as the spectroscopic data are included in the Supporting information.

### 2.2. Differential scanning calorimetry

The temperatures and the enthalpies of fusion of all halogenated derivatives 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 several reference materials (Santos et al., 2015; Almeida and Monte, 2016). For each compound, fresh samples sealed in aluminium crucibles were scanned from  $T = 298$  K to about 20 K above their temperature of fusion, at a heating rate of  $3.3 \cdot 10^{-2} \text{ K s}^{-1}$ , under a continuous nitrogen flux of  $0.8 \text{ mL s}^{-1}$ . No crystalline transitions were observed between 298.15 K and the melting temperatures of the compounds studied. The recorded thermograms were used to compute the onset temperatures of fusion,  $T_{\text{fus}}$ , and the enthalpies of fusion,  $\Delta_{\text{cr}}^{\text{H}}_m(T_{\text{fus}})$  reported in Table 2. The results determined in each of the individual runs are presented in the Supporting information (Table S1).

### 2.3. Vapor pressure measurements

In this work, two methods were used for the measurement of vapor pressures in complementary ranges at different temperatures: a mass loss effusion method, suitable for measuring pressures between 0.1 Pa and 1 Pa, and a static method, suitable for measuring pressures up to  $1.3 \cdot 10^3$  Pa.

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