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Vapor pressures, thermodynamic stability, and fluorescence properties of three 2,6-alkyl naphthalenes



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HIGHLIGHTS

determined.

temperatures.

were

⊿_fGm.

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• Thermodynamic and optical proper-

ties of 2,6-dialkyl naphthalenes were

• Vapor pressures of the compounds

• Thermodynamic stabilities of the compounds were evaluated from

• Quantum yields in the solid state and

in solution were determined.

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Naphthalene derivatives

Enthalpy of formation

Gibbs energy of formation

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at

different

measured

GRAPHICAL ABSTRACT

œŕ ∞^{\downarrow} 4.5 ∞ $E = \Delta_f H^0_m \qquad E = 0.29815 \Delta_f S^0_m$ $E = \Delta_f G_n^0$ 3.0 1000(K/T)

ABSTRACT

This work reports the experimental determination of relevant thermodynamic properties and the characterization of luminescence properties of the following polycyclic aromatic hydrocarbons (PAHs): 2,6-diethylnaphthalene, 2,6-diisopropylnaphthalene and 2,6-di-tert-butylnaphthalene. The standard $(p^{0} = 0.1 \text{ MPa})$ molar enthalpies of combustion, $\Delta_{c}H_{m}^{0}$, of the three compounds were determined using static bomb combustion calorimetry. The vapor pressures of the crystalline phase of 2,6diisopropylnaphthalene and 2,6-di-tert-butylnaphthalene were measured at different temperatures using the Knudsen effusion method and the vapor pressures of both liquid and crystalline phases of 2,6diethylnaphthalene were measured by means of a static method. The temperatures and the molar enthalpies of fusion of the three compounds were determined using differential scanning calorimetry. The gas-phase molar heat capacities and absolute entropies of the three 2.6-dialkylnaphthalenes studied were determined computationally. The thermodynamic stability of the compounds in both the crystalline and gaseous phases was evaluated by the determination of the Gibbs energies of formation and compared with the ones reported in the literature for 2,6-dimethylnaphthalene. From fluorescence spectroscopy measurements, the optical properties of the compounds studied and of naphthalene were evaluated in solution and in the solid state.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are recognized environmental contaminants that have been the focus of great concern due to their toxic and bio-accumulative effects. The major sources

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of PAHs in the environment originate from human activities, being mainly associated with oil spills, gas exploration, industrial discharges and incomplete combustion of organic materials. They have several industrial applications like starting materials, in which the alkyl groups lead to the corresponding dicarboxylic acids by oxidation. As promising monomers for the preparation of a variety of polymers (Hagen and Nemo, 1989; Takeuchi and Shimoura, 1998), they have been employed in the manufacture of films and fibers that reveal interesting heat resistance and mechanical properties. Alkylated naphthalenes have also been used as synthetic lubricating fluids with outstanding thermo-oxidative and hydrolytic stability, low volatility, and good solubility characteristics, offering advantages over other synthetic fluids like mineral base oils (Wu and Ho, 2006; Hourani et al., 2007).

PAHs are often resistant to biological degradation and are not efficiently removed by conventional physicochemical methods (Hinchee et al., 1994). They are dispersed in the atmosphere and show a great tendency to accumulate in living beings, soils, and sediments (Harvey, 1997). In humans, health risks associated with PAHs exposure include cancer and DNA damage (White, 1986; Luch, 2005). Naphthalene is the lowest molecular weight compound of the 16 PAHs present in the USEPA (United States Environmental Protection Agency) priority pollutant list (USEPA, 2014) and in the list of 45 priority regulated substances by the European Union (EU, 2013). Alkyl substituted naphthalenes are less volatile than their parent compound but their increasing hydrophobicity with the carbon number of the alkyl group contributes to their larger bioaccumulation in living beings and potentially pose enhanced toxicological effects (Scarlett et al., 2011).

The number, size, position and relative orientation of alkyl substituents of aromatic compounds influence their crystalline structure and several properties, such as solubility, volatility, and optoelectronic ones.

The relative abundance of PAHs in atmospheric air, water vapor and particulate matter is to a large extent conditioned by their volatility (Ravindra et al., 2008). The assessment of their thermodynamic stability is important to evaluate the reactivity of these compounds, in order to predict convenient chemical reactions leading to their degradation. Characterization of their fluorescence properties is necessary for the highly sensitive and selective analytical techniques that are widely used to identify PAHs (Mahanama et al., 1994; Rodríguez and Sanz, 2000; Huang et al., 2013; Ferretto et al., 2014). The present study is mainly focused on the evaluation of the volatility of the compounds studied (by measuring their vapor pressures at different temperatures), on the determination of their standard Gibbs energy of formation in the crystalline phase (a measure of the thermodynamic stability of the compounds), and on the characterization of their fluorescence properties.

2. Experimental

2.1. Compounds and purity control

The purity details and the provenance of the samples of naphthalene (CAS 91-20-3, $C_{10}H_8$), 2,6-diethylnaphthalene (CAS 59919-41-4, $C_{14}H_{16}$), 2,6-diisopropylnaphthalene (CAS 24157-81-1, $C_{16}H_{20}$) and 2,6-di-*tert*-butylnaphthalene (CAS 3905-64-4, $C_{18}H_{24}$) are summarized in Table S1, in the Supporting Information. The purity control of the samples was carried out 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. Their measured final mass fraction purities are, respectively,

0.9998, 0.9994, 0.9998 and 0.9993.

2.2. Differential scanning calorimetry

The temperatures and the enthalpies of fusion of the three compounds studied 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, five independent runs were performed. Fresh samples, sealed in aluminum crucibles, were scanned from T = 298 K to about 20 K above their temperature of fusion, at a heating rate of $3.3 \cdot 10^{-2}$ K s⁻¹, under a continuous nitrogen flux of 0.8 mL s⁻¹. The recorded thermograms were used to compute the onset temperatures of fusion, T_{fus} , and the enthalpies of fusion, $\Delta_{cr}^{1}H_m^{0}(T_{fus})$, of the three compounds.

2.3. Combustion calorimetry

The standard ($p^0 = 0.1$ MPa) massic energies of combustion of the three compounds were determined in an isoperibol static bomb calorimetric system, equipped with a stainless steel twin valve bomb (Parr 1108 model, internal volume of 0.342 dm³). The apparatus and the operating technique have been previously described (Ribeiro da Silva et al., 1984a, 1984b). Benzoic acid NIST Thermochemical Standard 39j, with a certified massic energy of combustion, under bomb conditions, of $-(26,434 \pm 3)$ J g⁻¹ (National Bureau of Standards, 1995) was used for calibration of the bomb. following the procedure described by Coops et al. (Coops et al., 1956). The value of the energy equivalent of the calorimeter, ϵ (calor) = (16002.6 ± 1.7) | K⁻¹, was determined as a mean of six calibration experiments, for an average mass of 3119.6 g of water added to the calorimeter (quoted uncertainty is the standard deviation of the mean). In all combustion experiments, the crystalline compounds were ignited in pellet form, at $T = (298.150 \pm 0.001)$ K, with 1.00 cm³ of deionised water and pressurized to 3.04 MPa with oxygen ($x_{02} \ge 0.99995$). 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 work (Santos et al., 2009; Santos and Ribeiro da Silva, 2009). The mass of compound, m(cpd), used in each experiment, and on which the energy of combustion was based, was determined from the mass of CO₂ produced (taking into account that formed from the combustion of the cotton thread fuse) and corrected from the apparent mass in air using the following density values, ρ /g cm⁻³: 0.974 (Chemnet, 2015a), 0.949 (Chemnet, 2015b), and 0.936 (Yaws and Chen, 2008), respectively, for 2,6-diethylnaphthalene, 2,6-diisopropylnaphthalene and 2,6di-tert-butvlnaphthalene.

At T = 298.15 K, $(\partial u/\partial p)_T$ was assumed to be -0.2 J g⁻¹ MPa⁻¹, for the compounds studied, a typical value for organic compounds (Washburn, 1933). Corrections to the standard state, ΔU_{Σ} , used for the calculation of the standard massic energy of combustion, $\Delta_c u^o$, were made following the procedure proposed by Hubbard et al. (Hubbard et al., 1956).

2.4. Vapor pressure measurements

The vapor pressure study of 2,6-diethylnaphthalene was performed using a static method which allowed the measurement of vapor pressures at different temperatures of both crystalline and liquid phases using a Baratron diaphragm capacitance gage (631A01TBEH) operating at a self-controlled constant temperature ($T_{gage} = 423$ K). This gage is suitable for measuring pressures in the Download English Version:

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