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Thermochemical properties of different 1-(R-phenyl)-1*H*-imidazoles

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ABSTRACT

Phenyl substituted imidazoles exhibit versatile biological activity. 1-(R-phenyl)-1*H*-imidazoles with different functional groups R provide a convenient suitcase of molecules with tunable physicochemical properties adjustable for many practical applications. In this work, the absolute vapor pressures of 1-(R-phenyl)-1*H*-imidazoles (with R = H, 2-methyl, 4-methyl, 2-methoxy, 4-methoxy, 2-fluoro, 4-fluoro, 2-bromo and 4-bromo) at different temperatures have been measured by the transpiration method for the first time. The standard enthalpies of vaporization of these compounds were derived from the temperature dependencies of the vapor pressures. An internal consistency of the standard vaporization enthalpies has been proven by comparison with vaporization enthalpies of parent species, as well as by a group contribution method. A system of group-additivity values is suggested for a quick assessment of vaporization enthalpies of different 1-(R-phenyl)-1*H*-imidazoles. Gas-phase standard molar enthalpies of formation of 1-(R-phenyl)-1*H*-imidazoles have been calculated using the high-level quantum-chemical method G3MP2. The combination of experimentally determined standard vaporization enthalpies with the G3MP2 results allows for the prediction of the liquid-phase standard enthalpies of formation for the studied compounds.

1. Introduction

Since Debus discovered the synthesis of 1*H*-imidazole by mixing glyoxal with ammonia [1] in the mid-19th century imidazole derivatives have taken over the organic chemistry world. The five-membered heterocyclic compounds are of great importance as they were found to be biologically active compounds with anti-inflammatory [2–4], anti-bacterial [5–7], anti-hypertensive [8] and even anti-cancer [9–11], and anti-viral [11] properties. They are also used as fungicides [2,5,6], herbicides [12] or plant-growth regulators [13,14] as well as ligands for organometallic complexes [15–20] and are the heterocyclic core for imidazolium based ionic liquids [21–24]. The first time phenyl substituted imidazoles were synthesized by Radziszewski in 1909 [25]. Since then many different ways to prepare 1-(R-phenyl)-1*H*-imidazoles were reported, for example by using hypervalent iodine species [26], coupling reactions with aryl halides [27,28] or aryl boronic acids [29,30] to name a few. In the following decades many different 1-(R-phenyl)-1*H*-imidazoles were synthesized [31–37] and up to today, new synthetic routes are published [38–40].

It is rather surprising that the research activities concentrated on the discovery of new synthetic routes and the investigation of their potential as medical and agriculture agents, but data on their physicochemical properties are absent in the literature. However, these data are crucial for the optimization of the synthetic routes as well as for the careful purification of substituted imidazoles before testing their versatile activities. In this work we report the results of systematic experimental and theoretical studies of thermodynamic properties for a group of eight *ortho*- and *para*-substituted 1-(R-phenyl)-1*H*-imidazole derivatives with methyl-, methoxy-, fluoro- and bromo-substituents (Fig. 1) and the unsubstituted 1-phenyl-1*H*-imidazole. The consistency of the experimental results has been proven by empirical and quantum-chemical methods.

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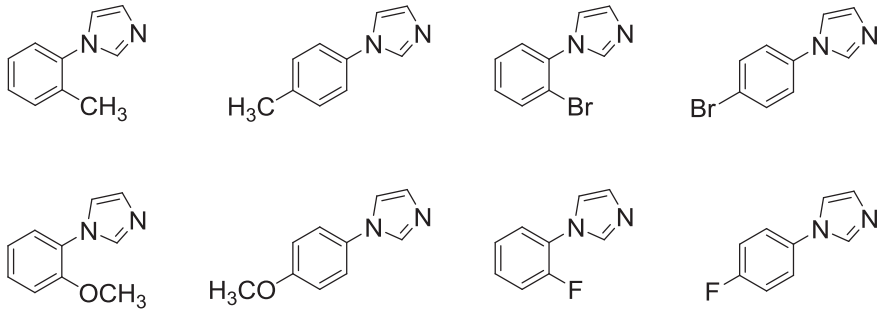

Fig. 1. Structures of methyl-, methoxy- and halogen-functionalized 1-(R-phenyl)-1*H*-imidazoles studied in this work.

2. Experimental section

2.1. Material synthesis

A sample of the 1-phenyl-1*H*-imidazole was of commercial origin (98%, TCI, CAS 7164-98-9). It was additionally purified by fractional distillation. Other samples of different 1-(R-phenyl)-1*H*-imidazoles [31–37] were prepared according to procedures described in detail in the Electronic Supplementary Material and purified especially for thermochemical studies. NMR data were recorded at room temperature on a Bruker AV-II 300 spectrometer operating at 300.1 MHz for ^{1}H, 75.5 MHz for ^{13}C and 282.4 MHz for ^{19}F and a Bruker DRX-500 P spectrometer operating at 500.1 MHz for ^{1}H, 125.8 MHz for ^{13}C. Chemical shifts δ are given in (ppm) relative to tetramethylsilane (TMS) with reference to solvent signals [^{1}H NMR: $CDCl_3$ (7.26); ^{13}C NMR: $CDCl_3$ (77.16)]. Signal patterns are indicated as *s* singlet; *d* doublet; *t* triplet; *q* quartet; *m* multiplet; *br* broad. Coupling constants *J* are given in Hertz (Hz). Elemental analysis of samples was performed by a Hekatech EA 3000 Euro Vector CHNSO elemental analyzer.

For each sample of the 1-(R-phenyl)-1*H*-imidazoles and also for the unsubstituted 1-(phenyl)-1*H*-imidazole used for thermochemical studies, the final degree of purity was determined by gas chromatography (Hewlett-Packard 5890 Series II) with flame ionization detector and a capillary column HP-5 with a column length of 30 m, an inside diameter of 0.32 mm, and a film thickness of 0.25 μm. The standard temperature program of the GC was $T = 333$ K for 180 s followed by a heating rate of 0.167 K s^{-1} to $T = 523$ K. The same GC conditions were used for the mass determinations in transpiration experiments. Provenance and purity of the compound prepared for thermochemical studies in this work are given in Table S1 (see Electronic Supplementary Material).

2.2. Vapor pressure measurements

2.2.1. Transpiration method

Temperature dependencies of absolute vapor pressures of 1-(R-phenyl)-1*H*-imidazoles were measured using the transpiration method [41,42]. At a constant temperature (T_i ± 0.1 K), a well-controlled N_2 stream was passed through the U-shaped saturator filled with a certain amount of a sample mixed with small glass beads. The material transported within a definite time was collected in a cold trap. The amount of condensed sample was determined by GC analysis using an external standard (*n*-tetradecane, $C_{14}H_{30}$). Vapor pressures (p_i) at each temperature (T_i) were calculated from the amount of the product, assuming the validity of Dalton's Law applied to the N_2 stream saturated with the substance *i*:

$$p_i = m_i \cdot R \cdot T_a / V \cdot M_i \quad V = V_{N2} + V_i \quad (V_{N2} \gg V_i) \tag{1}$$

where *R* is the ideal-gas constant; m_i is the mass of the condensed compound, M_i is the molar mass of compound *i*, and V_i is its volume contribution to the gaseous phase. V_{N2} is the volume of the carrier gas and T_a is the ambient temperature of the flowmeter. The N_2 gas flow rate was measured with the HP Agilent soap film flow meter (model 0101–0113). The volume of the carrier gas V_{N2} was calculated from the flow rate and the time measurements.

2.3. Computations

An initial search for stable conformers of the 1-(R-phenyl)-1*H*-imidazoles was performed with the force field MMFF94 method [43]. Energies of the most stable conformation of each molecule were calculated by the G3MP2 method [44] incorporated in the Gaussian 09 series of programs [45]. General computational details within this approach were reported elsewhere [46]. The enthalpy, H_{298}, of each compound was calculated according to standard thermodynamic procedures [47].

3. Results and discussion

3.1. Absolute vapor pressures

Vapor pressures of the 1-(R-phenyl)-1*H*-imidazoles measured at different temperatures are given in Table 1. They were fitted with the following equation [41]:

$$R \cdot \ln p/p^{\circ} = a + \frac{b}{T} + \Delta_l^g C_{p,m}^{\circ} \cdot \ln\left(\frac{T}{T_0}\right) \tag{2}$$

where *a* and *b* are adjustable parameters and T_0 is an arbitrarily chosen reference temperature (which has been chosen to be 298.15 K) and the reference pressure $p^{\circ} = 1$ Pa. The $\Delta_l^g C_{p,m}^{\circ}$ term is the difference of the molar heat capacities (in J·K^{-1}·mol^{-1}) of the gaseous and the liquid phases, respectively. Values of $\Delta_l^g C_{p,m}^{\circ}$ were calculated according to the procedure developed by Chickos and Acree [48]. The latter values were based on the heat capacities $C_{p,m}^{\circ}$(liq, 298.15 K) estimated by the group-contribution method [49]. Heat capacities and $\Delta_l^g C_{p,m}^{\circ}$-values are given in Table 2. Vapor pressures of the 1-(R-phenyl)-1*H*-imidazoles have been studied for the first time.

3.2. Enthalpies of vaporization

Vapor pressures of the 1-(R-phenyl)-1*H*-imidazoles were studied as close as possible to the reference temperature $T = 298.15$ K, in order to reduce uncertainties due to temperature adjustment.