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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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