

Energetics and Molecular Structure of 2,5-Dimethyl-1-phenylpyrrole and 2,5-Dimethyl-1-(4-nitrophenyl)pyrrole[†]

Manuel A. V. Ribeiro da Silva* and Ana Filipa L. O. M. Santos

Centro de Investigação em Química, Department of Chemistry, Faculty of Science, University of Porto, Rua do Campo Alegre, 687, P-4169-007 Porto, Portugal

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Thermochemical and thermodynamic properties of 2,5-dimethyl-1-phenylpyrrole and 2,5-dimethyl-1-(4-nitrophenyl)pyrrole have been determined by using a combination of calorimetric and effusion techniques as well as high-level ab initio molecular orbital calculations. The standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation, in the crystalline state, $\Delta_f H_m^\circ(\text{cr})$, at $T = 298.15$ K, were derived from the standard molar enthalpies of combustion, $\Delta_c H_m^\circ$, which were obtained from static bomb combustion calorimetry. The Knudsen mass-loss effusion technique was used to determine the standard molar enthalpies of sublimation, $\Delta_g H_m^\circ$, at $T = 298.15$ K. From the experimental results, the standard molar enthalpies of formation, in the gaseous phase, at $T = 298.15$ K, were derived. The results were analyzed and interpreted in terms of enthalpic increments and molecular structure. For comparison purposes, standard ab initio molecular calculations at the G3(MP2)//B3LYP level were performed, using a set of working reactions and the gas-phase enthalpies of formation of both compounds were estimated; the results are in excellent agreement with experimental data. The computational study was also extended to the determination of proton and electron affinities, basicities and adiabatic ionization enthalpies.

1. Introduction

During the last few decades, we have been focusing our attention on the thermochemistry of aromatic nitrogen heterocyclic containing compounds, being this paper a contribution to the thermochemical investigation of pyrrole derivatives, carried out on the Molecular Energetics, Colloids and Biointerfaces Research Group of University of Porto, following the studies of acetylpyrrole derivatives,^{1–3} pyrrolicarboxylic acids,⁴ and 1-phenylpyrrole and derivatives.^{5–7}

Thermochemical parameters, especially enthalpies of formation and bond dissociation enthalpies, are of crucial importance in establishing energetics–structure–reactivity relationships. These thermochemical parameters are fundamental to several fields ranging from chemistry, medicine, pharmaceutical sciences, biology, environmental, and industrial chemistry. They are needed to calculate the amount of energy involved in chemical reactions, to calculate other thermodynamic functions and to evaluate the stability of the molecules.

By its turn, the knowledge of vapor pressure values of pure substances, at different temperatures, allows the determination of several thermodynamic parameters such as enthalpies of sublimation. These parameters have assumed more relevance in the environmental area, since they determine the environmental purpose of chemical substances, their rate of evaporation in an industrial process or in dumps and to evaluate their behavior in the atmosphere.

The pyrrole molecule is a fundamental building block for biological systems, such as chlorophyll, hemoglobin, and cytochromes. The pyrrole-containing compounds are used in the synthesis of pharmaceuticals,^{8–16} dyes,^{17,18} agrochemicals,¹⁹ and other organic compounds.^{20–24} They also find technological applications such as catalysts, corrosion inhibitors, battery materials, and pacifying layers for semiconductors.²⁵

Alemán and collaborators reported a theoretical study of several 1-phenylpyrrole derivatives, obtained at the RHF/6-

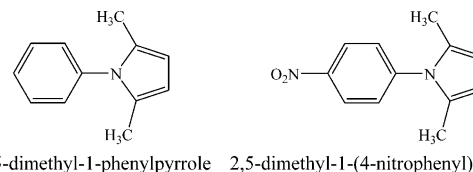


Figure 1. Structural formula of the compounds studied in this work.

31G(d) level,²⁶ and they found that the minimum energy conformation of 2,5-dimethyl-1-phenylpyrrole appears at a torsional angle, ϕ , of 90.0° .

The crystal structure of 2,5-dimethyl-1-(4-nitrophenyl)pyrrole was solved by Silva et al.²⁷ This molecule has a unit cell with a monoclinic, $P12_1/c1$ crystal system and crystallizes centrosymmetrically with two independent molecules in the asymmetric unit. In each molecule, the phenyl and pyrrole rings are mainly planar and their planes make an average angle of ca. 68.5° .

This work is devoted to study, both experimentally and theoretically, the energetics of 2,5-dimethyl-1-phenylpyrrole and 2,5-dimethyl-1-(4-nitrophenyl)pyrrole, whose structural formulas are depicted in Figure 1. The experimental studies were based on static bomb combustion calorimetric measurements, from which the standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation, in the crystalline phase, were calculated. Vapor pressure measurements at different temperatures using the Knudsen mass loss effusion technique enabled the determination of the enthalpies, entropies, and Gibbs energies of sublimation, at $T = 298.15$ K. From the experimental results, the standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation, in the gaseous phase, at $T = 298.15$ K, were derived.

The computational analysis of both title compounds, performed with the G3(MP2)//B3LYP approach, allow better knowledge of their molecular structure as well as the calculation of their gas-phase enthalpies of formation, using a set of gas-phase working reactions. The computational study was also extended to the determination of proton and electron affinities, basicities and adiabatic ionization enthalpies.

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* Corresponding author. Phone: +351-22-0402 521. Fax: +351-22-0402 522. E-mail: risilva@fc.up.pt.

We attempted also to analyze possible relationships between the structure and energetics of the compounds under study. For this purpose, an analysis of the experimental results in terms of enthalpic increments was carried out.

2. Experimental Section

2.1. Materials and Purity Control. The 2,5-dimethyl-1-phenylpyrrole [CAS 83-24-9] and 2,5-dimethyl-1-(4-nitrophenyl)pyrrole [CAS 5044-22-4] were purchased from Alfa-Aesar with assessed minimum massic fraction purities of 0.98 and 0.97, respectively.

These two compounds are crystals, at room temperature, and have been purified by successive sublimations under reduced pressure. The final purity of each one was checked by gas–liquid chromatography and by the consistent results obtained from the combustion experiments, as well as by the closeness to unity of the carbon dioxide recovery ratios. The average ratios of the mass of carbon dioxide recovered after combustion to that calculated from the mass of samples used in each experiment were 0.9998 ± 0.0012 for 2,5-dimethyl-1-phenylpyrrole and 1.0002 ± 0.0018 for 2,5-dimethyl-1-(4-nitrophenyl)pyrrole, where the uncertainties are twice the standard deviation of the mean.

The specific density used to calculate the true mass from the apparent mass in air of 2,5-dimethyl-1-phenylpyrrole was $\rho = 1.210 \text{ g}\cdot\text{cm}^{-3}$, calculated from the ratio mass/volume of a pellet of the compound (made in vacuum, with an applied pressure of $10^5 \text{ kg}\cdot\text{cm}^{-2}$) and for 2,5-dimethyl-1-(4-nitrophenyl)pyrrole the value used was $\rho = 1.253 \text{ g}\cdot\text{cm}^{-3}$.²⁷

2.2. Combustion Calorimetry. An isoperibol static bomb calorimeter, equipped with a Parr 1108 model twin valve bomb, made of stainless steel and with an internal volume of 0.342 dm^3 , was used to measure the enthalpies of combustion of both title compounds. The apparatus has been previously described.^{28,29}

The energy equivalent of the calorimeter was determined following the procedure described by Coops et al.,³⁰ from the combustion of benzoic acid (NIST Thermochemical Standard 39j), which has a certified massic energy of combustion, under bomb conditions, of $-26434 \pm 3 \text{ J}\cdot\text{g}^{-1}$.³¹ The value of the energy equivalent of the calorimeter was found to be $\varepsilon(\text{calor}) = 15995.3 \pm 2.0 \text{ J}\cdot\text{K}^{-1}$, as a mean of six calibration experiments, for an average mass of water added to the calorimeter of 3119.6 g ; the quoted uncertainty refers to the standard deviation of the mean.

For all experiments, samples in pellet form were ignited at $T = 298.150 \pm 0.001 \text{ K}$ in oxygen, at a pressure of 3.04 MPa , with a volume of 1.00 cm^3 of deionized water added to the bomb. The calorimeter temperatures were measured to $\pm 1 \times 10^{-4} \text{ K}$, at time intervals of 10 s , with a quartz crystal thermometer (Hewlett-Packard HP 2804 A), interfaced to a PC programmed to acquire data, control the calorimeter temperatures and to compute the adiabatic temperature change, through the program LABTERMO.³²

The electrical energy for ignition was determined from the change in potential difference across a capacitor ($1400 \mu\text{F}$) when discharged through a platinum ignition wire of diameter 0.05 mm . The massic energy of combustion of the cotton thread used as a fuse in all the experiments (empirical formula $\text{CH}_{1.686}\text{O}_{0.843}$) is $-16240 \text{ J}\cdot\text{g}^{-1}$;³³ this value has been previously confirmed in our laboratory. The nitric acid formed was determined by acid–base volumetry and corrections for it were based on $-59.7 \text{ kJ}\cdot\text{mol}^{-1}$ for the molar energy of formation of $0.1 \text{ mol}\cdot\text{dm}^{-3}$ $\text{HNO}_3(\text{aq})$ from $\text{N}_2(\text{g})$, $\text{O}_2(\text{g})$, and $\text{H}_2\text{O}(\text{l})$.³⁴ The amount of compound, $m(\text{cpd})$, used in each experiment and on which the energy of combustion was based, was determined from the total

mass of carbon dioxide produced by taking into account that formed from the combustion of the cotton thread fuse.

At $T = 298.15 \text{ K}$, $(\partial u/\partial p)_T$, for the two title studied compounds, was assumed to be $-0.2 \text{ J}\cdot\text{g}^{-1}\cdot\text{MPa}^{-1}$, a typical value for organic compounds.³⁵ The procedure given by Hubbard et al. was followed to obtain the corrections to the standard state, to calculate the standard massic energy of combustion, $\Delta_c u^\circ$.³⁶

The atomic weights used throughout this paper were those recommended by the IUPAC Commission in 2007.³⁷

2.3. Knudsen Effusion Technique. The vapor pressures of the two title compounds were measured as a function of temperature, through the mass-loss Knudsen effusion method. For 2,5-dimethyl-1-phenylpyrrole, due to its low melting point, an apparatus that enables work at temperatures below room temperature and the simultaneous operation of three Knudsen cells, with three different effusion orifices was used.³⁸ From now on, this apparatus will be named Knudsen-1. 2,5-Dimethyl-1-(4-nitrophenyl)pyrrole was studied in an apparatus that enables the simultaneous operation of nine aluminum effusion cells, which are placed in cylindrical holes inside three aluminum blocks, each one with three cells. Each block is maintained at a constant temperature, different from the other two blocks.³⁹ This apparatus will be referred to as Knudsen-2. For each compound, the measurements were extended through a selected temperature interval of ca. 20 K , chosen to correspond to measured vapor pressures in the range $0.1\text{--}1.0 \text{ Pa}$. In each effusion experiment, the loss of mass, Δm , of the samples, during a convenient effusion time period, t , is determined by weighing the effusion cells to $\pm 0.01 \text{ mg}$, before and after the effusion period, in a system evacuated to a pressure near $1 \times 10^{-4} \text{ Pa}$. At the temperature, T , of the experiment, the vapor pressure, p , is calculated by means of eq 1:

$$p = (\Delta m/A_o w_o t)(2\pi RT/M)^{1/2} \quad (1)$$

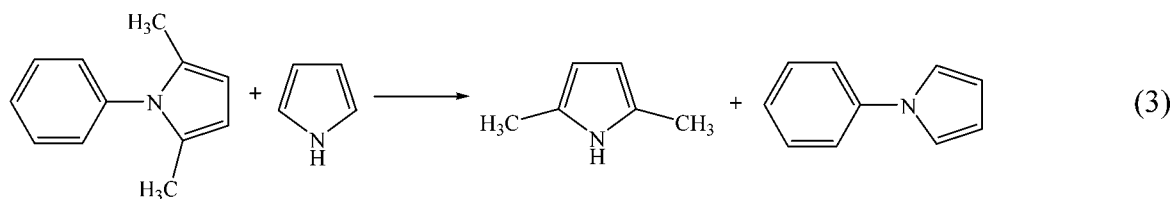
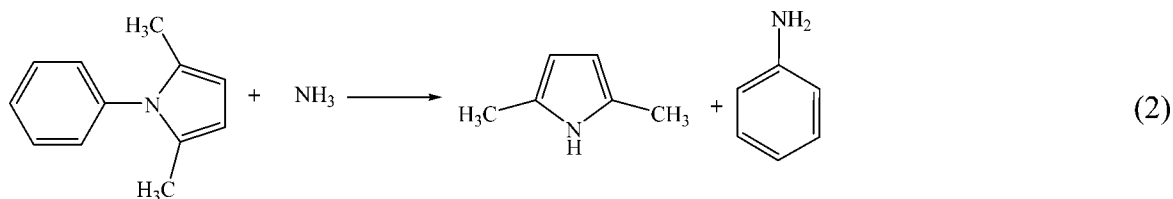
where A_o represents the area of the effusion orifice, w_o is the respective Clausing factor, R is the gas constant, and M is the molar mass of the effusing vapor.

For 2,5-dimethyl-1-phenylpyrrole, studied with the Knudsen-1 apparatus, the thickness of the effusion orifices was 0.0125 mm and their areas and Clausing factors were as follows: orifice 1, $A_o/\text{mm}^2 = 0.5053$, $w_o = 0.989$; orifice 2, $A_o/\text{mm}^2 = 0.7765$, $w_o = 0.991$; orifice 3, $A_o/\text{mm}^2 = 1.1370$, $w_o = 0.992$. For the Knudsen-2 apparatus, the areas and Clausing factors of the nine effusion orifices, made of platinum foil of 0.0125 mm thickness, are presented in the Supporting Information, Table S1.

3. Computational Details

The gas-phase standard molar enthalpies of formation of both studied compounds were estimated by computations based on standard ab initio molecular orbital calculations,⁴⁰ employing the G3(MP2)//B3LYP composite method.⁴¹ This approach uses the B3LYP/6-31G(d) level for geometry optimization and to compute thermal corrections for $T = 298.15 \text{ K}$, and the QCISD(T)/6-31G(d) and MP2/GTMP2Large approaches to obtain corrections to the energy calculated with the DFT method. The absolute enthalpies, at $T = 298.15 \text{ K}$, were obtained by adding the energies computed at $T = 0 \text{ K}$ with the vibrational, translational, rotational, and pV terms. All the computations were performed with the Gaussian 03 series of programs.⁴²

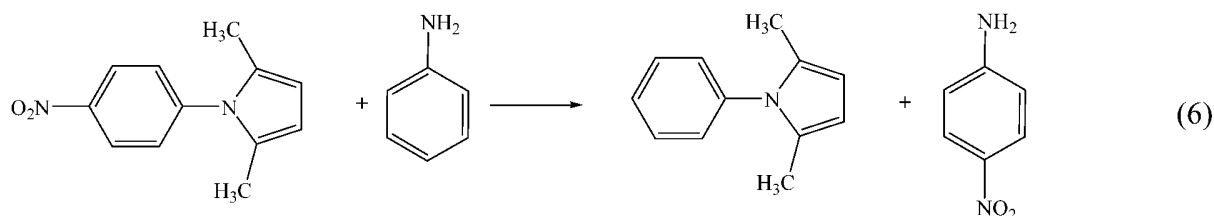
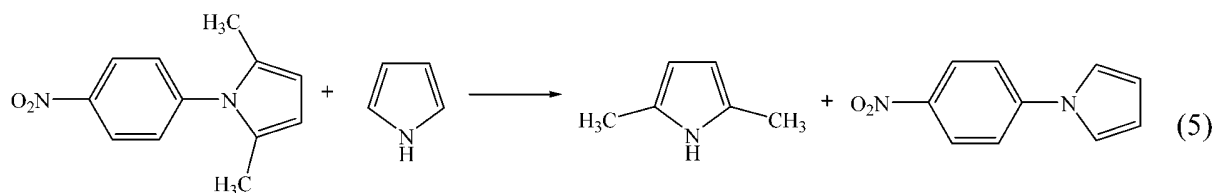
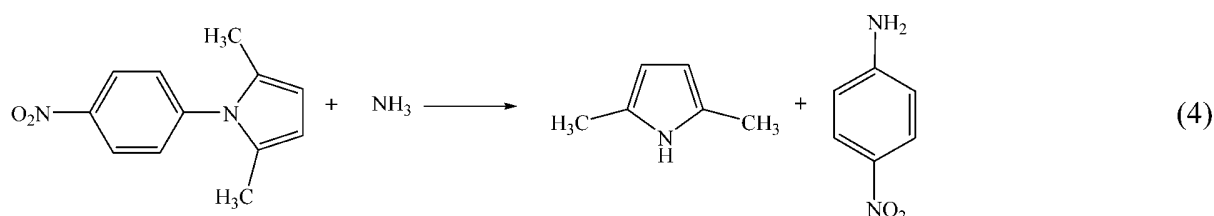
The enthalpy of formation of 2,5-dimethyl-1-phenylpyrrole was estimated considering the following gas-phase working reactions:



The gas-phase reactions presented below were used to estimate the enthalpy of formation of 2,5-dimethyl-1-(4-nitrophenyl)pyrrole:

4. Results and Discussion

4.1. Condensed Phase and Phase Transition. Results for



These reactions have been chosen by taking into consideration the availability of accurate experimental thermochemical data of the molecules there included.

The same composite approach was also used to calculate the proton and electron affinities, basicities, and adiabatic ionization enthalpies.

By convention, gas-phase basicity ($\Delta G_{\text{basicity}}$), proton affinity (PA), and electron affinity (EA) were calculated as



where A = 2,5-dimethyl-1-phenylpyrrole or 2,5-dimethyl-1-(4-nitrophenyl)pyrrole.

a typical combustion experiment of each compound are given in Table 1: $\Delta m(\text{H}_2\text{O})$ is the difference between the mass of water added to the calorimeter from 3119.6 g, the mass assigned for $\epsilon(\text{calor})$, ΔT_{ad} is the calorimeter temperature change corrected for the heat exchange and the work of stirring, ΔU_{Σ} is the correction to the standard state and the remaining terms are as previously defined.^{36,43} The internal energy for the isothermal bomb process, $\Delta U(\text{IBP})$, was calculated through eq 10:

$$\Delta U(\text{IBP}) = -\{\epsilon(\text{calor}) + c_p(\text{H}_2\text{O}, \text{l}) \cdot \Delta m(\text{H}_2\text{O}) + \epsilon_f\} \Delta T_{\text{ad}} + \Delta U(\text{ign}) \quad (10)$$

The detailed results for all the combustion experiments of each compound are presented in the Supporting Information, Tables S2 and S3.

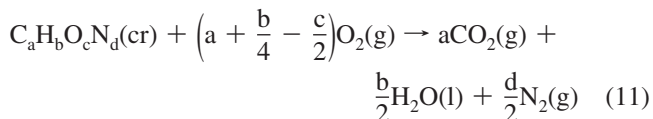
Table 2 lists the mean values of the standard ($p^\circ = 0.1 \text{ MPa}$) massic energy of combustion from six independent combustion

TABLE 1: Typical Combustion Results, at $T = 298.15$ K ($p^\circ = 0.1$ MPa), for the Studied Compounds^a

	2,5-dimethyl-1-phenylpyrrole	2,5-dimethyl-1-(4-nitrophenyl)pyrrole
$m(\text{CO}_2, \text{total})/\text{g}$	1.39722	1.00471
$m(\text{cpd})/\text{g}$	0.45126	0.40951
$m'(\text{fuse})/\text{g}$	0.00341	0.00283
$\Delta T_{\text{ad}}/\text{K}$	1.09958	0.77055
$\varepsilon_f/\text{J}\cdot\text{K}^{-1}$	15.70	15.03
$\Delta m(\text{H}_2\text{O})/\text{g}$	0.1	0
$-\Delta U(\text{IBP})/\text{J}$	17604.95	12335.81
$\Delta U(\text{fuse})/\text{J}$	55.38	45.96
$\Delta U(\text{HNO}_3)/\text{J}$	24.71	29.64
$\Delta U(\text{ign})/\text{J}$	0.89	0.95
$\Delta U_\Sigma/\text{J}$	9.04	7.89
$-\Delta_c u^\circ/\text{J}\cdot\text{g}^{-1}$	38815.36	29919.46

^a $m(\text{CO}_2, \text{total})$ is the mass of CO_2 recovered in each combustion; $m(\text{cpd})$ is the mass of compound burnt in each experiment; $m'(\text{fuse})$ is the mass of the fuse (cotton) used in each experiment; ΔT_{ad} is the corrected temperature rise; ε_f is the energy equivalent of the contents in the final state; $\Delta m(\text{H}_2\text{O})$ is the deviation of mass of water added to the calorimeter from 3119.6 g; $\Delta U(\text{IBP})$ is the energy change for the isothermal combustion reaction under actual bomb conditions and includes $\Delta U(\text{ignition})$; $\Delta U(\text{fuse})$ is the energy of combustion of the fuse (cotton); $\Delta U(\text{HNO}_3)$ is the energy correction for the nitric acid formation; $\Delta U(\text{ign})$ is the electric energy for the ignition; ΔU_Σ is the standard state correction; $\Delta_c u^\circ$ is the standard massic energy of combustion. ^b $\Delta U(\text{IBP})$ includes $\Delta U(\text{ignition})$.

experiments, $\langle \Delta_c u^\circ \rangle$, together with the standard deviations, the derived standard molar values for the energy, $\Delta_c U_m^\circ(\text{cr})$, and enthalpy, $\Delta_c H_m^\circ(\text{cr})$, of combustion as well as the standard molar enthalpies of formation, $\Delta_f H_m^\circ(\text{cr})$, in the crystalline phase, at $T = 298.15$ K, of 2,5-dimethyl-1-phenylpyrrole and 2,5-dimethyl-1-(4-nitrophenyl)pyrrole. The values of $\Delta_c u^\circ$ refer to the combustion reaction, represented by eq 11:



The uncertainties of the standard molar energies and enthalpies of combustion are twice the overall standard deviation of the mean and include the uncertainties in calibration and in the values of the auxiliary quantities used.^{44,45}

The values of $\Delta_f H_m^\circ(\text{cr})$, at $T = 298.15$ K, were calculated from $\Delta_c H_m^\circ(\text{cr})$, using the values of $\Delta_f H_m^\circ$ of $\text{H}_2\text{O}(\text{l})$, -285.830 ± 0.042 kJ·mol⁻¹, and $\text{CO}_2(\text{g})$, -393.51 ± 0.13 kJ·mol⁻¹.⁴⁶

The experimental results of the vapor pressure measurements at several temperatures, obtained from each effusion cell, together with the residuals of the Clausius–Clapeyron equation $\{10^2 \cdot \Delta \ln(p/\text{Pa})\}$, derived from least-squares adjustments are summarized in Tables 3 for 2,5-dimethyl-1-phenylpyrrole and Table 4 for 2,5-dimethyl-1-(4-nitrophenyl)pyrrole. The integrated form of the Clausius–Clapeyron equation, $\ln(p/\text{Pa}) = a$

TABLE 3: Knudsen Effusion Results for the 2,5-Dimethyl-1-phenylpyrrole

T/K	t/s	p/Pa			$10^2 \cdot \Delta \ln(p/\text{Pa})$		
		hole 1	hole 2	hole 3	hole 1	hole 2	hole 3
275.17	22174	0.119	0.112	0.116	5.3	−0.8	2.1
277.18	19738	0.145	0.149	0.142	−2.0	0.6	−4.1
279.18	17859	0.193	0.198	0.187	0.2	3.1	−2.8
281.16	16370	0.247	0.249	0.249	−0.4	0.2	0.2
283.12	11142	0.324	0.317	0.311	1.8	−0.4	−2.3
285.18	13182	0.408	0.398	0.394	−0.9	−3.4	−4.5
287.15	10999	0.554	0.535	0.534	5.2	1.7	1.6
289.19	11063	0.680	0.663	0.661	0.8	−1.7	−2.0
291.14	10781	0.877	0.854	0.842	2.9	0.1	−1.2
293.19	7378	1.122	1.079	1.073	3.1	−0.8	−1.3

$-b \cdot (T/\text{K})^{-1}$, where a is a constant and $b = \Delta_c^\circ H_m^\circ(\langle T \rangle)/R$, was used to derive the standard molar enthalpies of sublimation at the mean temperature of the experimental temperature range, $\langle T \rangle$. The equations obtained for 2,5-dimethyl-1-phenylpyrrole (12) and for 2,5-dimethyl-1-(4-nitrophenyl)pyrrole (13), together with the calculated standard deviations are as follows:

$$\ln p = (34.60 \pm 0.23) - \frac{10121 \pm 64}{T} \quad (12)$$

$$\ln p = (35.25 \pm 0.20) - \frac{12465 \pm 69}{T} \quad (13)$$

Table 5 presents the values of the standard ($p^\circ = 0.1$ MPa) molar enthalpies, $\Delta_c^\circ H_m^\circ$, entropies, $\Delta_c^\circ S_m^\circ$, and Gibbs energies $\Delta_c^\circ G_m^\circ$, of sublimation, at the mean temperature of the experiments $T = \langle T \rangle$ and at $T = 298.15$ K, for the two compounds under study.

The values of the enthalpies of sublimation, at $T = 298.15$ K, $\Delta_c^\circ H_m^\circ$, were calculated through eq 14, from the enthalpies of sublimation, at the mean temperature $\langle T \rangle$ of the experiment:

$$\Delta_c^\circ H_m^\circ(T=298.15\text{K}) = \Delta_c^\circ H_m^\circ(\langle T \rangle) + \Delta_c^\circ C_{p,m}^\circ(298.15 - \langle T \rangle) \quad (14)$$

For each compound studied, a value of -50 J·K⁻¹·mol⁻¹ for the $\Delta_c^\circ C_{p,m}^\circ$ was considered;⁴⁷ this value has already been used in previous works devoted to other pyrrole derivatives.^{1,3–7}

4.2. Gas-Phase Molecular Structures. The calculated structures of the most stable conformations of the 2,5-dimethyl-1-phenylpyrrole and 2,5-dimethyl-1-(4-nitrophenyl)pyrrole, optimized at the B3LYP/6-31G(d) level of theory (G3(MP2)//B3LYP calculations) are depicted in Figures 2 and 3, respectively. Selected bond distances and bond angles are also included. As was already noted for 1-phenylpyrrole and derivatives,^{5–7} the most stable conformation adopted by these two molecules was determined to be a twisted structure with dihedral angles between the phenyl and pyrrole planes of 71.3°, for 2,5-dimethyl-1-phenylpyrrole, and 60.0° for the 1-(4-nitrophenyl)

TABLE 2: Standard ($p^\circ = 0.1$ MPa) Massic Energies of Combustion, $\langle \Delta_c u^\circ \rangle$, Derived Standard Molar Energies of Combustion, $\Delta_c U_m^\circ$, Standard Molar Enthalpies of Combustion, $\Delta_c H_m^\circ$, and Standard Molar Enthalpies of Formation, $\Delta_f H_m^\circ$, for the Crystalline Compounds, at $T = 298.15$ K

compound	$-\langle \Delta_c u^\circ \rangle/\text{J}\cdot\text{g}^{-1}$ ^a	$-\Delta_c U_m^\circ(\text{cr})/\text{kJ}\cdot\text{mol}^{-1}$	$-\Delta_c H_m^\circ(\text{cr})/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_f H_m^\circ(\text{cr})/\text{kJ}\cdot\text{mol}^{-1}$
2,5-dimethyl-1-phenylpyrrole	38815.4 ± 2.6	6646.7 ± 2.4	6653.5 ± 2.4	73.5 ± 2.9
2,5-dimethyl-1-(4-nitrophenyl)pyrrole	29918.3 ± 1.7	6469.4 ± 2.3	6471.9 ± 2.3	34.8 ± 2.8

^a Mean value and standard deviation of the mean.

TABLE 4: Knudsen Effusion Results for the 2,5-Dimethyl-1-(4-nitrophenyl)pyrrole

<i>T</i> /K	<i>t</i> /s	orifices	<i>p</i> /Pa			$10^2 \cdot \Delta \ln(p/\text{Pa})$		
			small	medium	large	small	medium	large
331.11	22483	A1–B4–C7	0.0942	0.0926	0.0902	3.9	2.2	−0.4
333.13	22483	A2–B5–C8	0.118	0.115	0.111	3.2	1.2	−2.2
335.17	22483	A3–B6–C9	0.140	0.140	0.139	−2.4	−2.3	−3.2
337.11	18304	A1–B4–C7	0.181	0.182	0.178	2.0	2.6	0.6
339.14	18304	A2–B5–C8	0.225	0.222	0.218	1.6	0.3	−1.6
341.16	18304	A3–B6–C9	0.267	0.267	0.265	−3.1	−2.9	−3.5
343.11	14210	A1–B4–C7	0.345	0.344	0.336	1.9	1.5	−0.9
345.14	14210	A2–B5–C8	0.420	0.417	0.409	0.2	−0.4	−2.5
347.16	14210	A3–B6–C9	0.509	0.502	0.493	−1.5	−2.8	−4.6
349.12	10283	A1–B4–C7	0.651	0.659	0.642	2.9	4.2	1.5
351.14	10283	A2–B5–C8	0.797	0.804	0.772	2.6	3.5	−0.5
353.17	10283	A3–B6–C9	0.967	0.945	0.932	1.7	−0.7	−2.1

TABLE 5: Values of the Standard ($p^\circ = 0.1$ MPa) Molar Enthalpies, $\Delta_{\text{cr}}^\circ H_{\text{m}}^\circ$, Entropies, $\Delta_{\text{cr}}^\circ S_{\text{m}}^\circ$, and Gibbs Energies $\Delta_{\text{cr}}^\circ G_{\text{m}}^\circ$, of Sublimation, at the Mean Temperature of the Experiments $T = \langle T \rangle$ and $T = 298.15$ K, for the Compounds Studied

compound	$\langle T \rangle/\text{K}$	$\Delta_{\text{cr}}^\circ H_{\text{m}}^\circ(\langle T \rangle)/\text{kJ} \cdot \text{mol}^{-1}$	$\Delta_{\text{cr}}^\circ S_{\text{m}}^\circ(\langle T \rangle, p(\langle T \rangle))/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$T = 298.15$ K		
				$\Delta_{\text{cr}}^\circ H_{\text{m}}^\circ/\text{kJ} \cdot \text{mol}^{-1}$	$\Delta_{\text{cr}}^\circ S_{\text{m}}^\circ/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$\Delta_{\text{cr}}^\circ G_{\text{m}}^\circ/\text{kJ} \cdot \text{mol}^{-1}$
2,5-dimethyl-1-phenylpyrrole	284.18	84.2 ± 0.5	296.3 ± 1.8	83.5 ± 0.5	189.7 ± 1.8	26.9 ± 0.7
2,5-dimethyl-1-(4-nitrophenyl)pyrrole	342.14	103.6 ± 0.6	302.8 ± 1.8	105.8 ± 0.6	204.1 ± 1.8	44.9 ± 0.8

derivative. Adopting this conformation, the steric repulsions between the methyl substituents in the 2,5 positions of the pyrrole ring and the H atoms of the phenyl ring at the ortho positions are minimized. However, in these two molecules, the dihedral angles are much larger than the corresponding values of 36.3° and 30.1° found for 1-phenylpyrrole⁵ and 1-(4-nitrophenyl)pyrrole,⁶ respectively, where the absence of the two methyl substituents promotes a greater molecular stability and, consequently, a lower twist angle. It is worth noting that the large twisting between the two rings in 2,5-dimethyl-1-phenylpyrrole and 2,5-dimethyl-1-(4-nitrophenyl)pyrrole, induced by the methyl substituents in 2,5 positions, causes a high decrease of the conjugation effect, which provokes an increase of ca. 0.0010 nm the inter-ring bond length, toward the corresponding 1-phenylpyrrole and 1-(4-nitrophenyl)pyrrole.

Due to the electron-withdrawing character of the nitro group, the phenyl/pyrrole dihedral angle in 2,5-dimethyl-1-(4-nitrophenyl)pyrrole ($\phi = 60.0^\circ$) is ca. 11° lower than the corresponding one found for 2,5-dimethyl-1-phenylpyrrole ($\phi = 71.3^\circ$). This group causes a more efficient electron delocalization between the pyrrole and the phenyl rings, which is reflected by a C1–N1 bond length (0.1418 nm) in the 1-(4-nitrophenyl) derivative shorter than the one observed in the 2,5-dimethyl-1-phenylpyrrole (0.1427 nm).

In 2,5-dimethyl-1-phenylpyrrole, the rings are mainly planar, due to their aromatic nature; the torsion angle of the pyrrole ring (N1–C7–C8–C9–C10) is 0.2° and of the phenyl ring (C1–C2–C3–C4–C5–C6) is 0.3° ; a similar behavior was observed for 2,5-dimethyl-1-(4-nitrophenyl)pyrrole, in which the values are 0.6° and 0.7° , respectively. The NO₂ group is almost coplanar with the phenyl ring, as seen by the torsional angle O–N–C4–C3, 0.8° .

The values of the structural parameters found for 2,5-dimethyl-1-phenylpyrrole are in agreement with the ones obtained by Alemán et al. from ab initio RHF/6-31G(d).²⁶ However, they reported that the most stable conformation corresponds to a perpendicular arrangement, $\phi = 90.0^\circ$, ca. 19° higher than the twist angle found in this work. From X-ray studies, the phenyl/pyrrole dihedral angle in 2,5-dimethyl-1-(4-nitrophenyl)pyrrole was found to be 8.5° higher than the obtained by us, at the B3LYP/6-31G(d) level of theory.²⁷

4.3. Gas-Phase Experimental and Theoretical Enthalpies of Formation. The experimental values of the standard molar enthalpies of formation in the crystalline phase, $\Delta_{\text{f}}^\circ H_{\text{m}}^\circ(\text{cr})$, and of the standard molar enthalpies of sublimation, $\Delta_{\text{cr}}^\circ H_{\text{m}}^\circ(298.15 \text{ K})$, were used to derive the standard molar enthalpies of formation in the gaseous phase, $\Delta_{\text{f}}^\circ H_{\text{m}}^\circ(\text{g})$, of both studied compounds. These values are registered in Table 6.

To compare the experimental values derived in this work, we also calculated these parameters by means of computational thermochemistry. So, the standard molar enthalpies of formation of 2,5-dimethyl-1-phenylpyrrole and 2,5-dimethyl-1-(4-nitrophenyl)pyrrole were estimated by considering the computed enthalpies of reactions described by eqs 2 and 3 and 4–6, respectively, and the experimental enthalpies of formation in the gaseous phase of species there involved. The values of $\Delta_{\text{f}}^\circ H_{\text{m}}^\circ(\text{g})$ used were as follows: ammonia, $-45.90 \text{ kJ} \cdot \text{mol}^{-1}$;⁴⁸ pyrrole, $108.4 \pm 0.6 \text{ kJ} \cdot \text{mol}^{-1}$;⁴⁹ 2,5-dimethylpyrrole, $39.8 \pm 0.8 \text{ kJ} \cdot \text{mol}^{-1}$;⁴⁹ aniline, $87.1 \pm 1.1 \text{ kJ} \cdot \text{mol}^{-1}$;⁴⁹ 1-phenylpyrrole, $226.4 \pm 2.4 \text{ kJ} \cdot \text{mol}^{-1}$;⁵ *p*-nitroaniline, $58.8 \pm 1.5 \text{ kJ} \cdot \text{mol}^{-1}$;⁴⁹ 1-(4-nitrophenyl)pyrrole, $205.5 \pm 2.5 \text{ kJ} \cdot \text{mol}^{-1}$;⁶ 2,5-dimethyl-1-phenylpyrrole, $157.0 \pm 2.9 \text{ kJ} \cdot \text{mol}^{-1}$ (determined experimentally in this work). The calculated enthalpies of formation are listed and compared with the experimental results in Table 6. As can be seen in that table, the agreement between the reported experimental data and the G3(MP2)//B3LYP values is excellent. The maximum deviations from the experimental results do not exceed 1.8 and $2.9 \text{ kJ} \cdot \text{mol}^{-1}$, for 2,5-dimethyl-1-phenylpyrrole and its 1-(4-nitrophenyl) derivative, respectively. For all the working reactions, the differences obtained between the experimental and calculated data are smaller than the uncertainties associated to the experimental values.

In the case of 2,5-dimethyl-1-phenylpyrrole, the result calculated with eq 2 is almost identical to the experimental value. For 2,5-dimethyl-1-(4-nitrophenyl)pyrrole, eq 5 is the one that provides better estimates, being the deviation only $0.9 \text{ kJ} \cdot \text{mol}^{-1}$. A very good estimate is also obtained when reaction 6, which includes the value of $\Delta_{\text{f}}^\circ H_{\text{m}}^\circ(\text{g})$ of 2,5-dimethyl-1-phenylpyrrole determined experimentally in this work, is considered.

It is important to point out that, for both compounds, the use of different working reactions leads to estimated results that

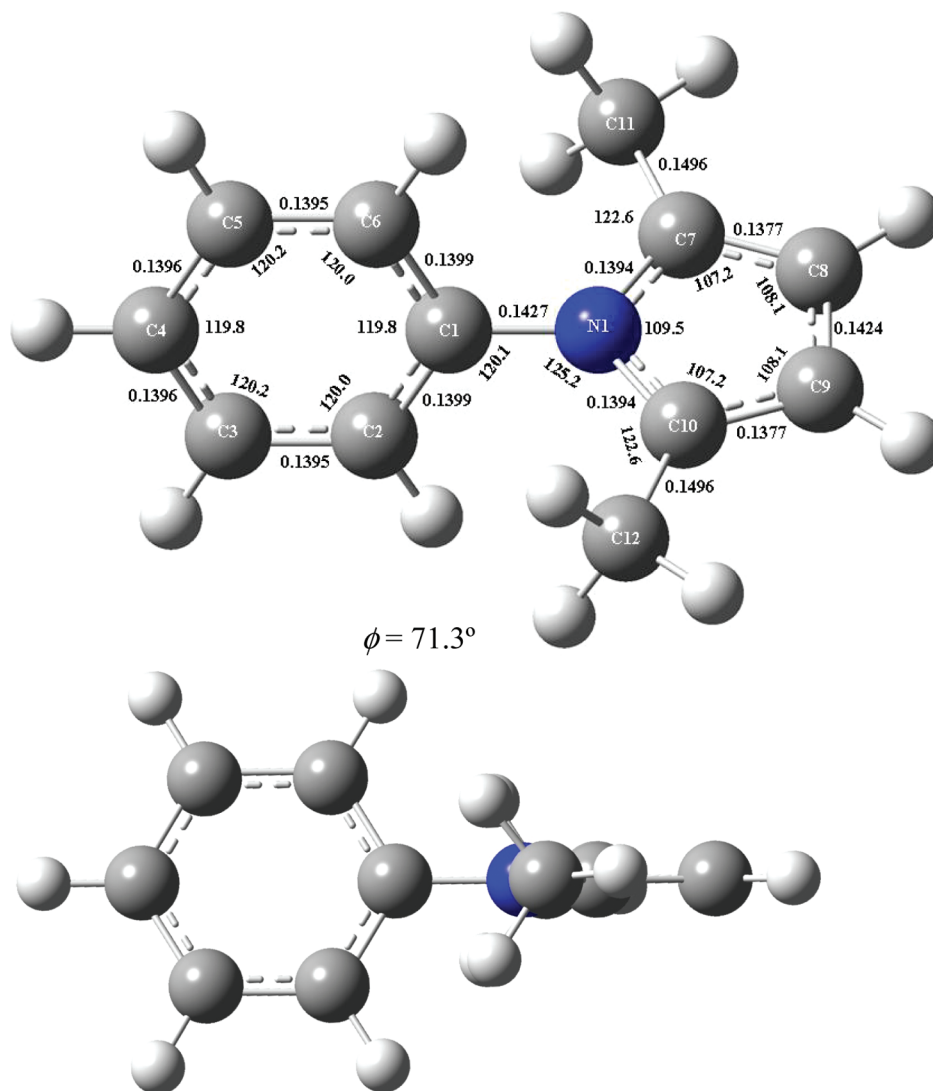


Figure 2. Front and side views of the B3LYP/6-31G(d) optimized structure of 2,5-dimethyl-1-phenylpyrrole. Selected bond lengths (nm) and bond angles (deg) are included.

are in excellent agreement with the experimental data obtained in this work.

The computed G3(MP2)//B3LYP enthalpies for the compounds under study and for the auxiliary molecules used in the several working reactions are listed in Table S4 in the Supporting Information.

The analysis of the enthalpic increments of the introduction of two methyl groups in the 2,5 positions of pyrrole and 1-phenylpyrrole is illustrated in Figure 4, schemes a and b, respectively. Those schemes clearly show that the stabilizer enthalpic increment of the substitution of two hydrogen atoms in the 2 and 5 positions of pyrrole and 1-phenylpyrrole by two methyl groups, to yield, respectively, the 2,5-dimethylpyrrole and the 2,5-dimethyl-1-phenylpyrrole, is equal, within the associated uncertainties, showing that the presence of the phenyl group does not cause additional enthalpic effects.

In the same way, it can be noticed that, within the associated experimental uncertainties, there are no enthalpic differences produced by the entrance of a nitro group in the fourth position of 1-phenylpyrrole and 2,5-dimethyl-1-phenylpyrrole, as shown in Figure 5. In both compounds, the introduction of the nitro group $-\text{NO}_2$ has a stabilizing effect, since it causes a more efficient electron delocalization between the pyrrole and the phenyl rings.

4.4. Other Gas-Phase Thermodynamic Properties. The G3(MP2)//B3LYP composite method was also applied in the determination of other thermodynamic properties for the 2,5-dimethyl-1-phenylpyrrole and 2,5-dimethyl-1-(4-nitrophenyl)pyrrole, namely, proton (PA) and electron affinities (EA), gas-phase basicities ($\Delta G_{\text{basicity}}$), and adiabatic ionization enthalpies (IE). All these quantities are summarized in Table 7. The introduction of one proton into each compound occurs at the same position in the ring, i.e., both molecules protonate, preferentially, on the C7 (=C10) position. The C1 atom was found to be their least favorable protonation site. When a $-\text{NO}_2$ group is introduced in the *p*-position of the phenyl ring of 2,5-dimethyl-1-phenylpyrrole, the proton affinity decreases by $31.8 \text{ kJ}\cdot\text{mol}^{-1}$.

The electron acceptor strength of a molecule is measured by its electron affinity; the greater the electron withdrawing power of the substituents, the better acceptor strength of the molecule. The value of the electron affinity obtained for the 2,5-dimethyl-1-phenylpyrrole is negative, which means that the electron capture is unfavorable. In opposite, the presence of the nitro group tends to increase the electron affinity of 2,5-dimethyl-1-(4-nitrophenyl)pyrrole to a large extent in comparison with 2,5-dimethyl-1-phenylpyrrole ($EA = 151.0 \text{ kJ}\cdot\text{mol}^{-1}$ vs $-50.5 \text{ kJ}\cdot\text{mol}^{-1}$, respectively). The presence of strong electron withdrawing substituents like $-\text{NO}_2$ enhances

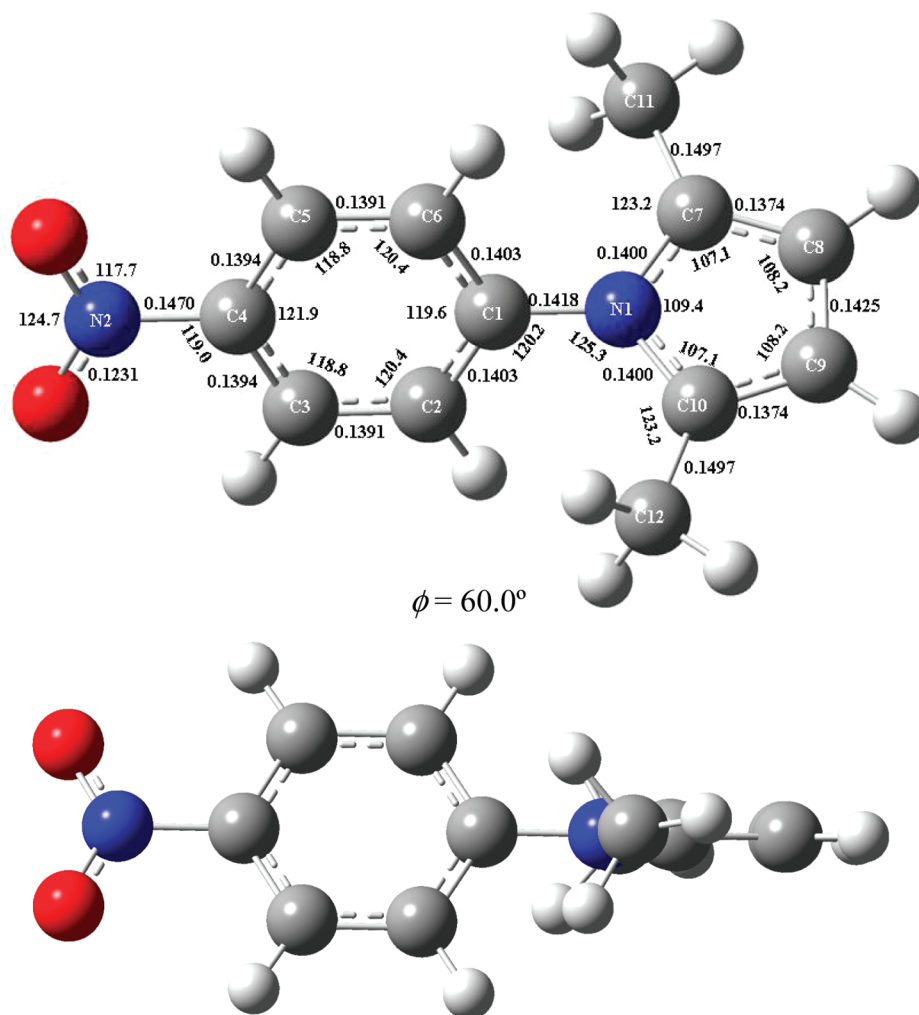


Figure 3. Front and side views of the B3LYP/6-31G(d) optimized structure of 2,5-dimethyl-1-(4-nitrophenyl)pyrrole. Selected bond lengths (nm) and bond angles (deg) are included.

TABLE 6: Comparison between the Experimental and Computed G3(MP2)//B3LYP Gas-Phase Enthalpies of Formation of 2,5-Dimethyl-1-phenylpyrrole and 2,5-Dimethyl-1-(4-nitrophenyl)pyrrole, at $T = 298.15$ K

compound	$\Delta_f H_m^\circ(\text{g})/\text{kJ} \cdot \text{mol}^{-1}$		
	experimental	G3(MP2)//B3LYP ^a	Δ^b
2,5-dimethyl-1-phenylpyrrole	157.0 ± 2.9	156.1 (2)	0.9
		158.8 (3)	-1.8
2,5-dimethyl-1-(4-nitrophenyl)pyrrole	140.6 ± 2.9	137.7 (4)	2.9
		139.7 (5)	0.9
		138.6 (6)	2.0

^a The respective working reactions are indicated in parentheses.

^b Difference between the experimental and computed values.

the electron affinity owing to the higher π conjugation in the anion, caused by the strong delocalization of an unpaired

electron (nitro derivatives possess very pronounced electron acceptor properties). The 2,5-dimethyl-1-(4-nitrophenyl)pyrrole is a strong acceptor and, by capturing one electron, it must form an anion more stable than the neutral molecule.

The calculated adiabatic ionization enthalpy for 2,5-dimethyl-1-(4-nitrophenyl)pyrrole is ca. $7 \text{ kJ} \cdot \text{mol}^{-1}$ more positive than the one obtained for 2,5-dimethyl-1-phenylpyrrole, which shows that a higher energy is required to remove an electron from the nitro derivative.

No experimental or computational data for these two compounds have been found in the literature for comparison with our results.

5. Conclusions

In the present work, the standard molar enthalpies of formation, in the gaseous phase, for 2,5-dimethyl-1-phenylpyrrole and 2,5-dimethyl-1-(4-nitrophenyl)pyrrole were determined

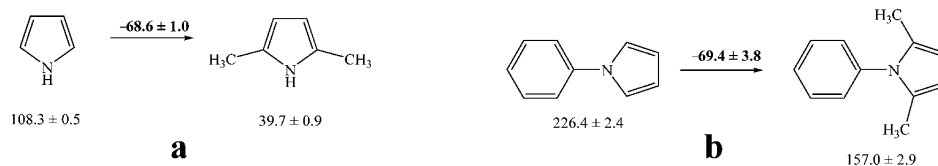


Figure 4. Enthalpic increments ($\text{kJ} \cdot \text{mol}^{-1}$) of the introduction of two $-\text{CH}_3$ groups in the 2,5 positions of (a) pyrrole and (b) 1-phenylpyrrole.

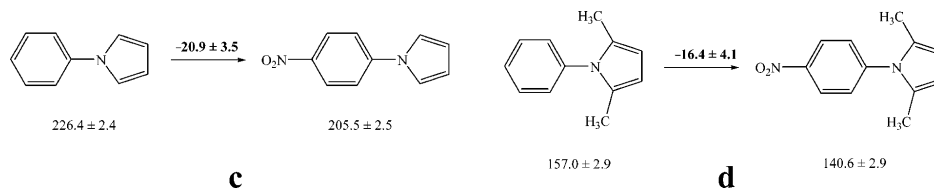


Figure 5. Enthalpic increments ($\text{kJ}\cdot\text{mol}^{-1}$) of the introduction of a $-\text{NO}_2$ group in the 4-position of (c) 1-phenylpyrrole and (d) 2,5-dimethyl-1-phenylpyrrole.

TABLE 7: G3(MP2)//B3LYP Computed Proton, PA, and Electron Affinities, EA, Gas-Phase Basicities, $\Delta G_{\text{basicity}}$, and Adiabatic Ionization Enthalpies, IE, at $T = 298.15$ K, for 2,5-Dimethyl-1-phenylpyrrole and 2,5-Dimethyl-1-(4-nitrophenyl)pyrrole (All Values in $\text{kJ}\cdot\text{mol}^{-1}$)

compound	PA	$\Delta G_{\text{basicity}}$	EA	IE
2,5-dimethyl-1-phenylpyrrole	943.3 (C7 = C10)	906.3	-50.5	700.6
2,5-dimethyl-1-(4-nitrophenyl)pyrrole	911.5 (C7 = C10)	879.4	151.0 ^a	708.0 ^b

^a B3LYP/6-311+G(2d,2p) value due to convergence problems in G3(MP2)//B3LYP calculations for the anion. ^b B3LYP/6-311+G(2d,2p) value due to convergence problems in G3(MP2)//B3LYP calculations for the cation.

by experimental (static bomb combustion calorimetry and Knudsen effusion technique) and computational methods (G3(MP2)//B3LYP approach). The experimental values obtained were, respectively, 157.0 ± 2.9 and $140.6 \pm 2.9 \text{ kJ}\cdot\text{mol}^{-1}$, and using different working reactions, a perfect agreement with the calculated data was achieved. Furthermore, other thermodynamic properties of these molecules were also calculated by means of the G3(MP2)//B3LYP composite method. At the B3LYP/6-31G(d) level of theory the molecular structures of both compounds under study have been established and the structural parameters have been obtained. From an analysis of the experimental results obtained in this work, in terms of enthalpic increments, it was shown that they correlate well between each other and with available literature values for structural related compounds.

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Supporting Information Available: Detailed data of the effusion orifices (diameter and Clausing factors) of the Knudsen-2 apparatus, the data and the details of all the combustion calorimetry experiments for the 2,5-dimethyl-1-phenylpyrrole and 2,5-dimethyl-1-(4-nitrophenyl)pyrrole and, G3(MP2)//B3LYP enthalpies (energies plus thermal corrections for $T = 298.15$ K) for the 2,5-dimethyl-1-phenylpyrrole and for 2,5-dimethyl-1-(4-nitrophenyl)pyrrole as well as for the auxiliary molecules used in the several working reactions are presented in the Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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