Molecular energetics of pyrrolecarbonitriles and derivatives: A combined calorimetric and computational study

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ABSTRACT

In this work, calorimetric measurements were carried out, in order to determine the standard (p^o = 0.1 MPa) molar enthalpies of formation, in the gaseous phase, $\Delta_f H_m^o$(g), at T = 298.15 K, of 2-pyrrolecarbonitrile and 1,5-dimethyl-2-pyrrolecarbonitrile. These data were calculated from the standard molar enthalpies of formation, in the condensed phase, $\Delta_f H_m^o$(cr, l), at T = 298.15 K, derived from static bomb combustion calorimetry measurements, and from the standard molar enthalpies of phase transition, $\Delta_{cr,l}^g H_m^o$, at T = 298.15 K, obtained by high temperature Calvet microcalorimetry. The gas-phase enthalpies of formation were also calculated from high level *ab initio* molecular orbital calculations, at the G3(MP2)//B3LYP level, and a very good agreement between experimental and computational values was obtained, giving us support to estimate the gas-phase enthalpies of formation of 3-pyrrolecarbonitrile and 1,5-dimethyl-3-pyrrolecarbonitrile. Moreover, the molecular structure of the four molecules was established and the structural parameters were determined at the B3LYP/6-31G(d) level of theory.

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1. Introduction

Pyrrole derivatives represent a class of compounds of great importance in heterocyclic chemistry. They constitute the structural feature of many biologically important molecules, which include the hemoglobin, chlorophyll, porphyrins, corrins, vitamin B_{12} and the bile pigments [1–4].During the last years, we have directed our attention towards the understanding of the molecular and energetic properties of this kind of compounds, their stability and reactivity, as well as their energetics-structure relationships, by studying the thermochemical and thermophysical properties of pyrrole derivatives [5–14], both experimental and computationally, owing to its role as building blocks of the naturally-occurring porphyrins, the tetrapyrrolic "pigments of life", and due to the relevance of the molecule and its derivatives in the synthesis of organic polymers [15–17], dyes [18,19], agrochemicals [20] or other organic compounds [21–25].

As a continuation of the systematic work that we have been carrying out, the present study is focused on the molecular energetics of pyrrolecarbonitriles and derivatives. The 2-pyrrolecarbonitrile derivatives are key compounds in the synthesis porphobilinogen, the main building block used in the biosynthesis of the "pigments

of life" [26–28]. The tetrapyrrolic compounds have been applied in photodynamic therapy for the treatment of cancer [29,30]. The 2-pyrrolecarbonitrile finds application in organometallic chemistry [31] and it is present in tobacco and tobacco smoke [32,33]. The 3-pyrrolecarbonitrile moiety was found to impart antibacterial activity; it is presented in compounds with antibacterial activity *in vitro* against Gram-positive and Gram-negative pathogens and that are effective *in vivo* against *S. aureus* and *S. pneumoniae* [34]. Fensome and collaborators [35] synthesized a compound in which pyrrolecarbonitriles moieties are presented; these compounds demonstrated potent activity on progesterone receptor antagonist, that can be potential contraceptive agents.

In this paper, the experimental and computational standard (p^o = 0.1 MPa) molar enthalpies of formation, in the gaseous phase, at T = 298.15 K, of 2-pyrrolecarbonitrile and 1,5-dimethyl-2-pyrrolecarbonitrile, whose structural formulas are depicted in figure 1, are reported. These values were derived from the standard molar enthalpies of formation, in the condensed phase, obtained by static bomb combustion calorimetry and from their standard molar enthalpies of phase transition, determined by high temperature Calvet microcalorimetry.

High-level *ab initio* molecular orbital calculations, at the G3(MP2)//B3LYP level, were performed and the estimated gas-phase enthalpies of formation of 2-pyrrolecarbonitrile and 1,5-dimethyl-2-pyrrolecarbonitrile were obtained. These calculations

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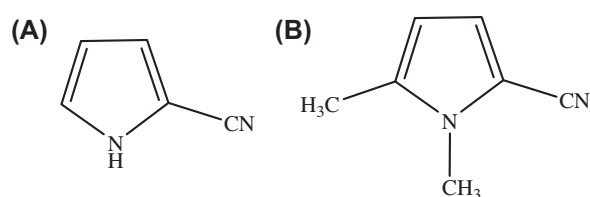
FIGURE 1. Structural formulas for 2-pyrrolecarbonitrile (A) and 1,5- dimethyl-2-pyrrolecarbonitrile (B).

were further extended to the 3-pyrrolecarbonitrile and 1,5-di-methyl-3-pyrrolecarbonitrile that were not studied experimentally. The molecular structures of the four molecules were also established.

2. Experimental

2.1. Compounds and purity control

The origin and purification details of the samples of 2-pyrrole-carbonitrile and 1,5-dimethyl-2-pyrrolecarbonitrile used in this work are summarized in table 1.

The final purity of both compounds was also checked by the percentage of carbon dioxide recovered during the combustion experiments. The average ratios of the mass of carbon dioxide recovered to those calculated from the mass of samples used in each experiment, together with the uncertainties (twice the standard deviation of the mean) were: 2-pyrrolecarbonitrile (0.9993 ± 0.0001); 1,5-dimethyl-2-pyrrolecarbonitrile (1.0001 ± 0.0002).

According to the certificate of analysis given by Sigma-Aldrich Chemical Co., the sample of 2-pyrrolecarbonitrile used in this work has 0.004 molar fraction of water, determined by Karl–Fischer titration. After purification, we have analysed our sample and the molar fraction of water obtained by Karl-Fischer titration was only (0.00084 ± 0.00008).

The values of the specific densities, ρ = 1.081 g · cm^{-3} for 2-pyr-rolecarbonitrile [36] and ρ = 1.066 g · cm^{-3} for 1,5-dimethyl-2-pyrrolecarbonitrile [37] were used, and the relative atomic masses used for the elements were the ones recommended by the IUPAC Commission in 2009 [38].

2.2. Combustion calorimetry

The enthalpies of combustion of the compounds 2-pyrrolecar-bonitrile and 1,5-dimethyl-2-pyrrolecarbonitrile were measured in an isoperibol static bomb calorimeter, equipped with a twin valve bomb made of stainless steel and with an internal volume of 0.342 dm^3 [39,40].

The calorimetric system was calibrated with benzoic acid NIST Standard Reference Material, sample 39j, with a certified massic energy of combustion, when burnt under the bomb conditions, of −(26434 ± 3) J · g^{-1} [41]. The energy equivalent of the calorimeter was determined as ε(calor) = (15995.3 ± 2.0) J · 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 the

standard deviation of the mean. The calibration procedure was the one suggested by Coops et al. [42].

The crystalline samples of benzoic acid and of 1,5-dimethyl-2-pyrrolecarbonitrile were ignited in pellet form, while the liquid 2-pyrrolecarbonitrile was burnt enclosed in previously weighed polyester bags made of Melinex, 0.025 mm of thickness. The energy of combustion of the melinex used in each experiment, ΔU(melinex), was calculated using the value of the massic energy of combustion of dry melinex, $\Delta_c u^o$ = −(22902 ± 5) J · g^{-1} [43], after making the correction for the mass fraction of water, w = 0.0032 [43]. The mass of carbon dioxide produced from the combustion of melinex was calculated using the factor previously reported [43].

The compounds were ignited in oxygen, at T = (298.150 ± 0.001) K, under a pressure of 3.04 MPa, with 1.00 cm^3 of deionised water introduced into the bomb. The calorimeter temperatures were collected every 10 s, with a precision of ±(1 · 10^{-4}) K, using a quartz crystal thermometer (Hewlett Packard HP 2804 A), interfaced to a PC programmed to data acquisition and to compute the adiabatic temperature change, by means of the LABTERMO program [44].

The electrical energy for ignition was determined from the change in potential difference across a 1400 µF capacitor when dis-charged through a platinum ignition wire (diameter ϕ = 0.05 mm). For the cotton thread fuse, empirical formula CH$_{1.686}$O$_{0.843}$, $\Delta_c u^o$ = −16240 J · g^{-1} [45], a value which has been previously con-firmed in our laboratory.

The amount of nitric acid produced was quantified by acid-base volumetry and the respective correction was based on −59.7 kJ · mol^{-1} for the standard molar energy of formation of 0.1 mol · dm^{-3} HNO3(aq), from N$_2$(g), O$_2$(g) and H$_2$O(l) [46]. The quantity of compound, m(cpd), used in each experiment and on which the energy of combustion was based, was determined from the mass of CO$_2$ produced, taking into account that formed from the combustion of the cotton thread fuse and of the Melinex (for the combustion experiments of 2-pyrrolecarbonitrile).

At T = 298.15 K, a pressure coefficient of specific energy, $(\partial u / \partial p)_T$, was assumed to be −0.2 J · g^{-1} · MPa^{-1}, a common value for organic compounds [47].

Corrections to the standard state were made following the pro-cedure proposed by Hubbard et al. [48].

2.3. High temperature Calvet microcalorimetry

The standard molar enthalpies of phase transition of the two compounds studied were measured in a high temperature Calvet microcalorimeter (Setaram, model HT 1000), through the drop-microcalorimetric technique for vacuum sublimation, described by Skinner et al. [49], for the sublimation of solid compounds and adapted, in our Laboratory, for liquid vaporizations [50]. The details of the apparatus and the technique have been previously described [51].

The calibration of the microcalorimeter was made using the reported standard molar enthalpy of sublimation of naphthalene (Aldrich, mass fraction purity > 0.99), $\Delta_{cr}^g H_m^o$ (298.15 K) = (72.6 ± 0.6) kJ · mol^{-1} [52], and of vaporization of n-undecane (Aldrich, mass fraction purity > 0.99), $\Delta_l^g H_m^o$ (298.15 K) m= (56.580 ± 0.566) kJ · mol^{-1} [52].

TABLE 1
Purification details of the studied compounds.

Chemical name	CAS	Provenance	Initial molar fraction purity	Purification method	Final molar fraction purity	Analysis method
2-Pyrrolecarbonitrile (l)	4513-94-4	Aldrich Chemical Co.	0.99	Distillation	0.9995	GC[a]
1,5-Dimethyl-2-pyrrolecarbonitrile (cr)	56341-36-7	Aldrich Chemical Co.	0.99	Sublimation	0.9999	GC[a]

[a] Gas–liquid chromatography.

The calibration constants, k, of the calorimeter were obtained as the average of six independent experiments for the predefined temperatures, $k(T = 340 \text{ K}) = 1.0072 \pm 0.0018$ for the vaporization experiments of the 2-pyrrolecarbonitrile and $k(T = 350 \text{ K}) = 1.0006 \pm 0.0025$ for the sublimation experiments of the 1,5-dimethyl-2-pyrrolecarbonitrile; the uncertainties presented are the standard deviations of the mean.

The samples with a mass of 4 to 6 mg of solid compound, or 6 to 9 mg of liquid compound, were introduced in thin glass capillary tubes sealed at one end and weighed with a precision of $\pm (1 \cdot 10^{-6}) \text{ g}$. The sample and the blank reference capillary tubes were simultaneously dropped into the hot reaction cells, kept at a suitable predefined temperature T, and then removed from the hot zone by vacuum sublimation or vaporization.

The thermal corrections for the differences in the mass of both capillary tubes and different sensibilities of the two measuring cells were obtained by making separate blank correction experiments, dropping empty tubes of nearly equal mass into each of the twin cells [51].
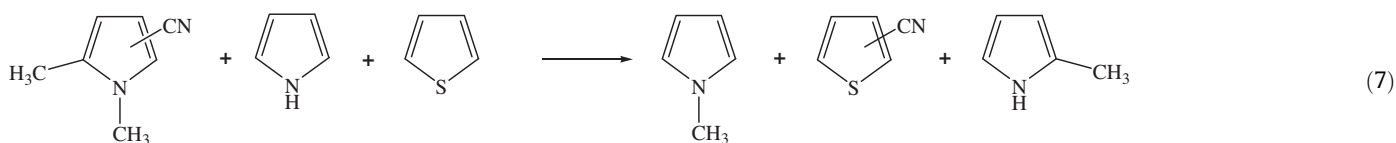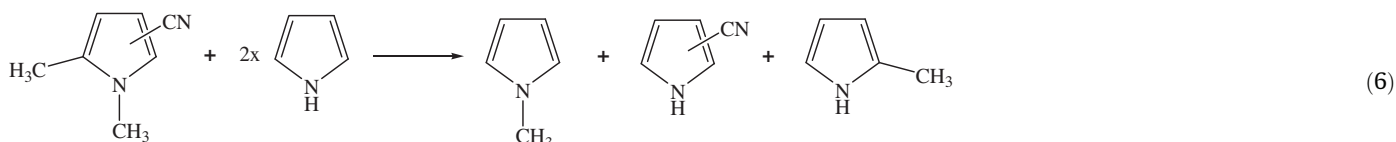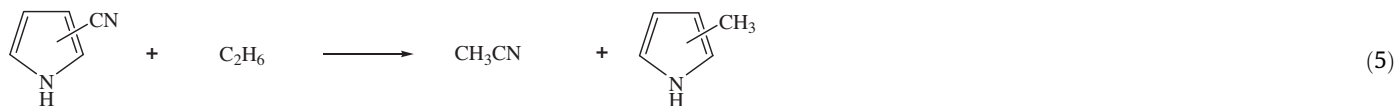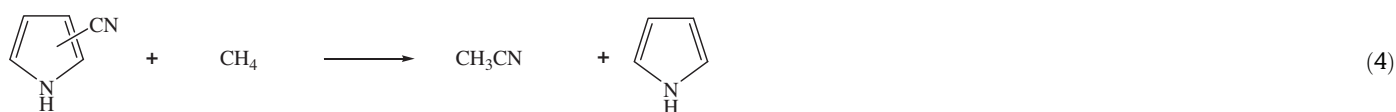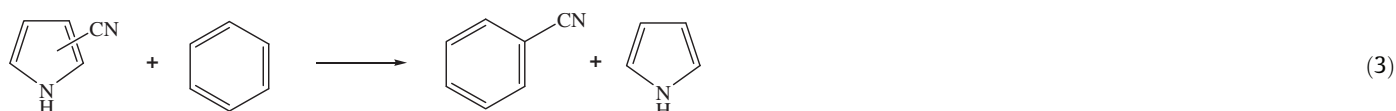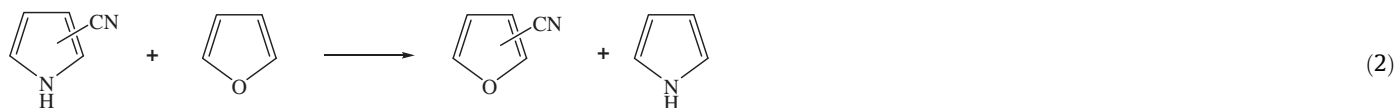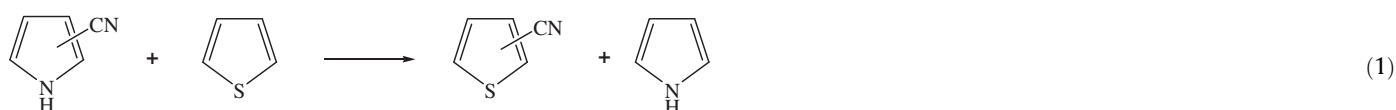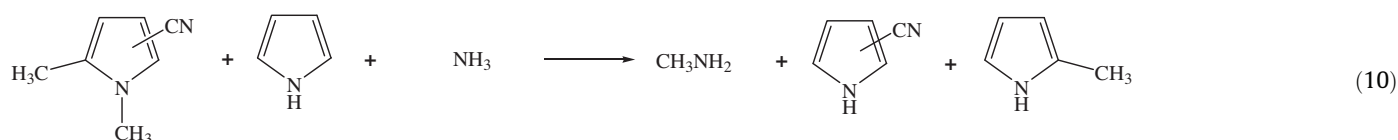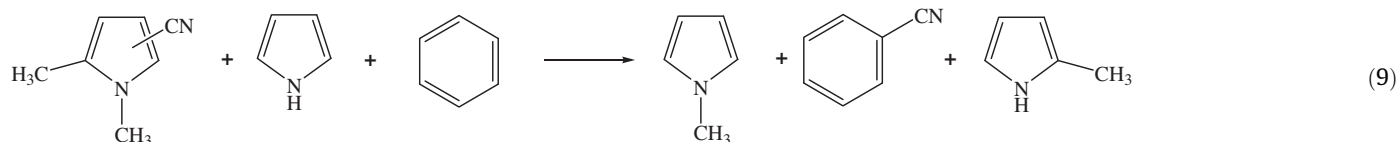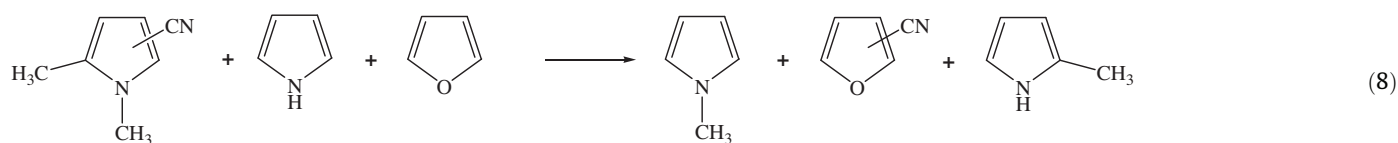
3. Computational thermochemistry

The standard *ab initio* molecular orbital calculations for the 2- and 3-pyrrolecarbonitriles, 1,5-dimethyl-2- and 1,5-dimethyl-3-pyrrolecarbonitriles were performed with Gaussian 03 computer code [53], and the composite G3(MP2)//B3LYP approach was the methodology employed [54]. In this method, the geometry full-optimization and calculation of the frequencies of the molecule are done through the hybrid B3LYP method together with the split-valence polarized 6-31G(d) basis set. The zero-point energies (ZPEs) are obtained from B3LYP/6-31G(d) calculations, with a scale factor of 0.96. Then, single-point calculations are carried out at higher levels of electronic structure theory: quadratic configuration interaction (QCISD(T)) and the 2nd-order Moller–Plesset (MP2) with, respectively, the 6-31G(d) and GTMP2Large basis set.

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 the pV terms computed at the B3LYP/6-31G(d) level of theory.

These enthalpies, at $T = 298.15 \text{ K}$, were then used to estimate the enthalpy of formation of the compounds studied experimentally, by combining the enthalpy of the gas-phase working reactions 1 to 5 for the 2-pyrrolecarbonitrile and 6 to 10 for the 1,5-dimethyl-2-pyrrolecarbonitrile and the experimental enthalpies of formation of the molecules there involved. The calculations were also extended to the respective 3-isomers that were not studied experimentally.

(1)

(2)

(3)

(4)

(5)

(6)

(7)

$$\text{(reaction scheme)} \tag{8}$$

$$\text{(reaction scheme)} \tag{9}$$

$$\text{(reaction scheme)} \tag{10}$$

4. Experimental results

The results of one combustion experiment of each compound studied are given in table 2. The internal energy associated to the isothermal bomb process, $\Delta U(\text{IBP})$, was calculated through:

$$\Delta U(\text{IBP}) = -\{\varepsilon(\text{calor}) + c_p(\text{H}_2\text{O}, \text{l}) \cdot \Delta m(\text{H}_2\text{O}) + \varepsilon_f\}\Delta T_{\text{ad}} + \Delta U(\text{ign}) \tag{11}$$

where $c_p(\text{H}_2\text{O},\text{l})$ is the massic heat capacity, at constant pressure, for the liquid water, $\Delta m(\text{H}_2\text{O})$ represents the difference between the mass of water added to the calorimeter and the mass assigned for $\varepsilon(\text{calor})$ (3119.6 g), ε_f is the energy equivalent of the bomb content in the final state, ΔT_{ad} is the calorimeter temperature change corrected for the heat exchange and the work of stirring and $\Delta U(\text{ign})$ is the electrical energy for ignition.
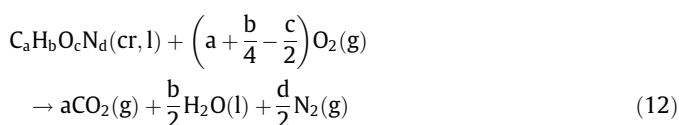
The individual values of $\Delta_c u^o$, together with the respective mean value, $\langle \Delta_c u^o \rangle$, and their standard deviations are presented in table 3. These values are referred to the general idealized combustion reaction represented by equation (12):

$$\text{C}_a\text{H}_b\text{O}_c\text{N}_d(\text{cr}, \text{l}) + \left(a + \frac{b}{4} - \frac{c}{2}\right)\text{O}_2(\text{g})$$

$$\rightarrow a\text{CO}_2(\text{g}) + \frac{b}{2}\text{H}_2\text{O}(\text{l}) + \frac{d}{2}\text{N}_2(\text{g}) \tag{12}$$

Detailed information of each combustion experiment, for the compounds studied, are given in the supporting information, tables S1 and S2.

The derived standard molar values for the energy, $\Delta_c U_m^o(\text{cr}, \text{l})$, and enthalpy of combustion, $\Delta_c H_m^o(\text{cr}, \text{l})$, as well as the standard molar enthalpies of formation, in the condensed phase, $\Delta_f H_m^o(\text{cr}, \text{l})$, at $T = 298.15$ K, for the two compounds studied experimentally, are presented in table 4. The $\Delta_f H_m^o(\text{cr}, \text{l})$ for each compound was calculated from the respective $\Delta_c H_m^o(\text{cr}, \text{l})$ and from the standard molar

TABLE 2
Typical combustion results, at T = 298.15 K, (p° = 0.1 MPa), for the studied compounds.

	2-Pyrrolecarbonitrile	1,5-Dimethyl-2-pyrrolecarbonitrile
$m(\text{CO}_2, \text{total})/\text{g}$	1.85221	1.74450
$m(\text{cpd})/\text{g}$	0.73177	0.67847
$m'(\text{fuse})/\text{g}$	0.00267	0.00305
$m''(\text{melinex})/\text{g}$	0.04345	
$\Delta T_{\text{ad}}/\text{K}$	1.41642	1.42020
$\varepsilon_f/\text{J} \cdot \text{K}^{-1}$	15.35	15.75
$\Delta m(\text{H}_2\text{O})/\text{g}$	0	0
$-\Delta U(\text{IBP})^a/\text{J}$	22676.70	22737.91
$\Delta U(\text{fuse})/\text{J}$	43.36	49.53
$\Delta U(\text{melinex})/\text{J}$	995.12	
$\Delta U(\text{HNO}_3)/\text{J}$	73.91	57.30
$\Delta U(\text{ign})/\text{J}$	1.10	0.98
$\Delta U_\Sigma/\text{J}$	17.91	14.20
$-\Delta_c u^o/\text{J} \cdot \text{g}^{-1}$	29444.22	33335.12

$m(\text{CO}_2, \text{total})$ 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; $m''(\text{melinex})$ is the mass of melinex used as auxiliary of combustion; 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); $\Delta U(\text{melinex})$ is the energy of combustion of melinex used as auxiliary of combustion; $\Delta U(\text{HNO}_3)$ 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; $\Delta_c u^o$ is the standard massic energy of combustion.

^{a} $\Delta U(\text{IBP})$ includes $\Delta U(\text{ignition})$.

TABLE 3
Individual values of standard (p^o = 0.1 MPa) massic energies of combustion, $\Delta_c u^o$, of the compounds, at T = 298.15 K.

2-Pyrrolecarbonitrile	1,5-Dimethyl-2-pyrrolecarbonitrile
	$-\Delta_c u^o/(\text{J} \cdot \text{g}^{-1})$
29430.35	33338.03
29444.22	33335.12
29460.86	33347.74
29449.81	33332.39
29448.52	33325.95
29436.12	33345.90
	$-\langle \Delta_c u^o \rangle/(\text{J} \cdot \text{g}^{-1})^a$
$(29445.0 \pm 4.4)^a$	$(33337.5 \pm 3.4)^a$

^{a} Mean value and standard deviation of the mean.

TABLE 4
Derived standard (p° = 0.1 MPa) molar values for the compounds studied, at T = 298.15 K.

Compound	$\dfrac{-\Delta_c U_m^o(\text{cr}, \text{l})}{\text{kJ} \cdot \text{mol}^{-1}}$	$\dfrac{-\Delta_c H_m^o(\text{cr}, \text{l})}{\text{kJ} \cdot \text{mol}^{-1}}$	$\dfrac{\Delta_f H_m^o(\text{cr}, \text{l})}{\text{kJ} \cdot \text{mol}^{-1}}$
2-Pyrrolecarbonitrile (l)	2711.8 ± 1.4	2711.8 ± 1.4	172.6 ± 1.5
1,5-Dimethyl-2-pyrrolecarbonitrile (cr)	4005.6 ± 1.6	4008.1 ± 1.6	110.2 ± 1.8

TABLE 5

Standard ($p° = 0.1$ MPa) molar enthalpies of phase transition, $\Delta_{cr,l}^{g}H_m^o$ for the two compounds, at $T = 298.15$ K, determined by Calvet microcalorimetry.

Compound	Number of experiments	$\dfrac{T}{K}$	$\dfrac{\Delta_{cr,l}^{g}H_m^o}{kJ \cdot mol^{-1}}$	$\dfrac{\Delta_{298.15\,K}^{T}H_m^o(g)}{kJ \cdot mol^{-1}}$	$\dfrac{\Delta_{cr,l}^{g}H_m^o (298.15\,K)}{kJ \cdot mol^{-1}}$
2-Pyrrolecarbonitrile (l)	5	339.6	69.5 ± 0.2	4.2710 ± 0.0007	65.3 ± 1.4
1,5-Dimethyl-2-pyrrolecarbonitrile (cr)	5	350.2	86.3 ± 0.5	8.0669 ± 0.0015	78.3 ± 1.6

enthalpies formation, at $T = 298.15$ K, of H$_2$O (l), $-(285.830 \pm 0.042)$ kJ · mol^{-1} and CO$_2$ (g), $-(393.51 \pm 0.13)$ kJ · mol^{-1} [55].

According to Rossini [56] and Olofsson [57], the uncertainties assigned to the standard molar energy and enthalpy of combustion are twice the overall standard deviation of the mean, including the contribution from the calibration with benzoic acid and from the values of the auxiliary quantities used.

The results obtained from the microcalorimetric measurements of the enthalpies of sublimation or vaporization, for the compounds studied, are presented in table 5. The corrective term $\Delta_{298.15\,K}^{T}H_m^o(g)$, calculated through the equation (13), was used to correct the enthalpies of phase transition, at the experimental temperature T, to $T = 298.15$ K:

$$\Delta_{298.15\,K}^{T}H_m^o(g) = \int_{298.15\,K}^{T} C_{p,m}^o(g)dT. \tag{13}$$

The gas-phase molar heat capacities of 2-pyrrolecarbonitrile (equation (14)) and 1,5-dimethyl-2-pyrrolecarbonitrile (equation (15)) were determined computationally by means of DFT calculations, using the B3LYP approach and the 6-31G(d) basis set (vibrational frequencies scaled by a factor of 0.9614) [58]. The $C_{p,m}^o(g) = f (T)$ for 2-pyrrolecarbonitrile and 1,5-dimethyl-2-pyrrolecarbonitrile, between 150 and 600 K, are listed in the supporting information, table S3.

$$
\begin{aligned}
C_{p,m}^o(g)/(J \cdot K^{-1} \cdot mol^{-1}) = &-2.88027 \cdot 10^{-7}(T/K)^3 \\
&+ 1.39986 \cdot 10^{-4}(T/K)^2 \\
&+ 2.66050 \cdot 10^{-1}(T/K) \\
&+ 13.3285(R^2 = 0.99988),
\end{aligned}
$$

$$
\begin{aligned}
C_{p,m}^o(g)/(J \cdot K^{-1} \cdot mol^{-1}) = &-3.81567 \cdot 10^{-7}(T/K)^3 \\
&+ 2.65502 \cdot 10^{-4}(T/K)^2 \\
&+ 3.13937 \cdot 10^{-1}(T/K) \\
&+ 38.334(R^2 = 0.99998).
\end{aligned}
$$

In table 5, the uncertainties associated with the values of $\Delta_{cr,l}^{g}H_m^o (298.15\,K)$ are twice the overall standard deviation of the mean and include the uncertainties in calibration and in the gas-phase molar heat capacity.

5. Discussion

5.1. Computational Section: Molecular structures and enthalpies of formation

The calculated molecular structures of 2-pyrrolecarbonitrile, 3-pyrrolecarbonitrile, 1,5-dimethyl-2-pyrrolecarbonitrile and 1,5-dimethyl-3-pyrrolecarbonitrile, optimized at the B3LYP/6-31G(d) level of theory (G3(MP2)//B3LYP calculations), are shown in figure 2, in which the selected bond distances and bond angles are included. The 3-pyrrolecarbonitrile is planar, pertaining to the symmetry point group C_s, while the 2-isomer is almost planar (C4C3C2C6 = 179.95°), symmetry point group C_1. Due to the strong electron-withdrawing character of the –CN group, the π-conjugation in the pyrrole ring can be affected, causing some changes in

the strength of the adjacent bonds to the atoms in which the –CN group is attached and, consequently, an alteration of the bond lengths. For instance, C3–C4 in 3-pyrrolecarbonitrile (0.1434 nm) and in 1,5-dimethyl-3-pyrrolecarbonitrile (0.1431 nm) is higher than in the corresponding 2-isomers, i.e., this bond is weaker than in 2-pyrrolecarbonitrile (0.1414 nm) and 1,5-dimethyl-2-pyrrolecarbonitrile (0.1410 nm) due to the proximity of the –CN group, that removes electronic density from the ring. Similar behaviour can be observed for the 2-pyrrolecarbonitrile and 1,5-dimethyl-2-pyrrolecarbonitrile, in which the N1-C2 bond length is greater than for the 3-isomers. The introduction of a carbonitrile group in the pyrrole ring, either in the 2- or 3-positions increases, slightly, the N1-H bond length, by 0.0001 nm (N-H bond length in pyrrole is 0.1008 nm) [5].

There are in the literature some structural data for the pyrrolecarbonitriles. Rimarčik and collaborators [59] performed a theoretical study of the structure and electronic properties of cyano-substituted pyrroles with the PBE0/TZVP and MP2/TZVP approaches, and Su [60] carried out a computational study on the photochemical isomerization reactions of cyanopyrroles, with the CAS(8,7)/6-311G(d,p) method; they have obtained the structural parameters of 2- and 3-pyrrolecarbonitriles, which are in satisfactory agreement with the corresponding ones obtained in this work.

No structural data for the 1,5-dimethylpyrrolecarbonitriles have been found in the literature for comparison with our results.

The experimentally derived standard molar enthalpies of formation, in the gaseous phase, $\Delta_f H_m^o$ (g), at $T = 298.15$ K, for the two compounds studied, are summarized in table 6. In this table are also registered the computational gas-phase molar enthalpies of formation of 2-pyrrolecarbonitrile and 1,5-dimethyl-2-pyrrolecarbonitrile, estimated by combining the enthalpy of reactions 1 to 5 and 6 to 10, respectively, and the corresponding atomization reaction, at $T = 298.15$ K, computed at the G3(MP2)//B3LYP level, with the experimental enthalpies of formation of the auxiliary molecules and atoms used. All the experimental values of $\Delta_f H_m^o$ (g) for the auxiliary species involved in the working reactions are presented in table S4, in the supporting information.

From the data collected in table 6, we can observe that the estimated values for the 2-pyrrolecarbonitrile and 1,5-dimethyl-2-pyrrolecarbonitrile are in excellent agreement with the experimental ones, with deviation of only 0.1 kJ · mol^{-1} and 1.1 kJ · mol^{-1}, respectively. In both cases, the maximum deviations obtained are smaller than the uncertainty associated with the experimental values and it should be highlighted that several working reactions lead to estimated results that fit very well with the experimental values, giving them reliability and clearly showing that the composite G3(MP2)//B3LYP method seem to work very well with this type of compounds, as it was already seen in previous works. The experimental value of $\Delta_f H_m^o$ (g) obtained in this work for the 2-pyrrolecarbonitrile was used in the working reactions 6 and 10 to estimate the $\Delta_f H_m^o$ (g) of 1,5-dimethyl-2-pyrrolecarbonitrile, yielding calculated values that differs only by 1.3 and 1.5 kJ · mol^{-1}, respectively, from the experimental one which, once more, gives confidence to our results. In this way, these computations were extended to the calculation of the $\Delta_f H_m^o$(g) of the 3-isomers, i.e., the 3-pyrrolecarbonitrile and 1,5-dimethyl-3-pyrrolecarbonitrile, using the gas-phase enthalpies of reactions 1 to 5 and 6 to 10, respectively, as well as the atomization reactions. The results are summarized in table 6 which shows that
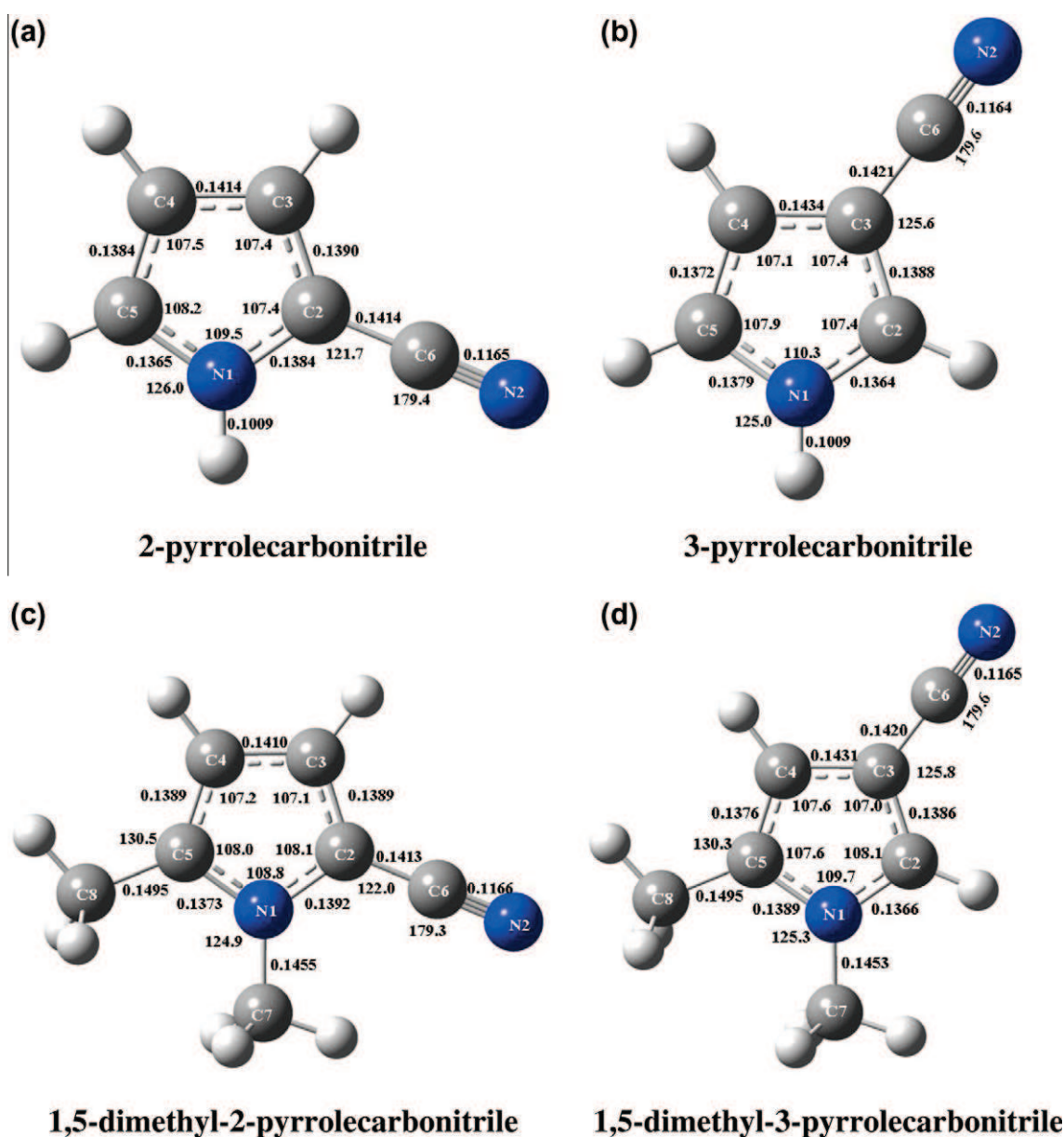
FIGURE 2. B3LYP/6-31G(d) optimized most stable configurations for the 2-pyrrolecarbonitrile, 3-pyrrolecarbonitrile, 1,5-dimethyl-2-pyrrolecarbonitrile and 1,5-dimethyl-3-pyrrolecarbonitrile. Selected bond lengths (nm) and bond angles (deg) are included.

TABLE 6
Experimental and G3(MP2)//B3LYP computed gas-phase enthalpies of formation, of the pyrrolecarbonitrile derivatives, at $T = 298.15$ K.[a]

Reaction	2-Pyrrolecarbonitrile	3-Pyrrolecarbonitrile	reaction	1,5-Dimethyl-2-pyrrolecarbonitrile	1,5-Dimethyl-3-pyrrolecarbonitrile
			$\dfrac{\Delta_f H_m^o(\mathrm{g})}{\mathrm{kJ \cdot mol^{-1}}}$		
1	238.4 (−0.5)	232.0	6	189.8 (−1.3)	187.4
2	238.1 (−0.2)	231.3	7	190.2 (−1.7)	187.2
3	238.9 (−1.0)	233.1	8	190.0 (−1.5)	186.5
4	237.8 (0.1)	232.0	9	190.7 (−2.2)	188.3
5	239.2 (−1.3)	233.4	10	187.0 (1.5)	184.6
Atom.	237.0 (0.9)	231.2	Atom.	187.4 (1.1)	184.9
Exp.	237.9 ± 2.1			188.5 ± 2.4	

[a] Enthalpic differences between the experimental and computed values are given in parentheses.

similar calculated values are obtained applying different working reactions; thus, mean values for the $\Delta_f H_m^o$ (g) of 3-pyrrolecarbonitrile and 1,5-dimethyl-3-pyrrolecarbonitrile are defined as 232.2 kJ · mol^{-1} and 186.5 kJ · mol^{-1}, respectively.

The calculated values by the G3(MP2)//B3LYP method can have an average absolute deviation as large as 5.2 kJ · mol^{-1} [54]. Despite the average absolute deviation of the values calculated by the G3(MP2)//B3LYP, the data obtained by using the different

working reactions (table 6) are much closer among them, and with the experimental result, than this possible deviation would allow.

The computed G3(MP2)//B3LYP enthalpies for the compounds studied, auxiliary molecules and atoms used in the atomization and working reactions are presented in table S4 in the supporting information and in table S5 is given the **e**stimated gas-phase enthalpy of formation, at T = 298.15 K, for 3-furancarbonitrile.

6. Conclusions

In the present work, the standard molar enthalpies of formation, in the gaseous phase, for 2-pyrrolecarbonitrile and 1,5-dimethyl-2-pyrrolecarbonitrile were determined by experimental (static bomb combustion calorimetry and Calvet microcalorimetry) and computational methods (G3(MP2)//B3LYP approach). The experimental values obtained were, respectively, (237.9 ± 2.1) $kJ \cdot mol^{-1}$ and $(188.5 \pm 2.4) \, kJ \cdot mol^{-1}$, and using different working reactions, a perfect agreement with the calculated data was obtained. The computational calculations were extended to the 3-pyrrolecarbonitrile and 1,5-dimethyl-3-pyrrolecarbonitrile and mean computational $\Delta_f H_m^o$ (g) values were obtained. At the B3LYP/6-31G(d) level of theory the molecular structures of the four compounds have been established and the structural parameters have been obtained.

Acknowledgments

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jct.2011.12.019.

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