# A Combined Experimental and Computational Thermodynamic Study of the Isomers of Pyrrolecarboxaldehyde and 1-Methyl- pyrrolecarboxaldehyde

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

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

S *Supporting Information*

ABSTRACT: The present paper reports an experimental calorimetric study of 2-pyrrolecarboxaldehyde and 1-methyl-2-pyrrolecarboxaldehyde, which aims to determine their standard ($p° = 0.1$ MPa) molar enthalpies of formation, in the gaseous phase, at $T = 298.15$ K. These values were derived from the standard ($p° = 0.1$ MPa) molar enthalpies of formation, in the condensed phase, $\Delta_f H_m°(cr,l)$, at $T = 298.15$ K, obtained from the standard molar enthalpies of combustion, $\Delta_c H_m°$, measured by static bomb combustion calorimetry, and from the standard molar enthalpies of phase transition, $\Delta_{cr,l}^g H_m°$ at $T = 298.15$ K, obtained by high temperature Calvet micro-calorimetry. Additionally, the standard enthalpies of formation of these two compounds were estimated by computations based on standard ab initio molecular calculations at the G3(MP2)//B3LYP level. The estimated values are in very good agreement with experimental data, giving us support to estimate the gas-phase enthalpies of formation of the 3-pyrrolecarboxaldehyde and 1-methyl-3-pyrrolecarboxaldehyde that were not studied experimentally. N—H bond dissociation enthalpies, gas-phase acidities and basicities, proton and electron affinities, and adiabatic ionization enthalpies were also calculated. Furthermore, the molecular structure of the four molecules was established and the structural parameters were determined at the B3LYP/6-31G(d) level of theory.

$\Delta_r H(\text{calc}) = 12.9$ kJ·mol^{-1}

$\Delta_r H(\text{calc}) = 9.8$ kJ·mol^{-1}
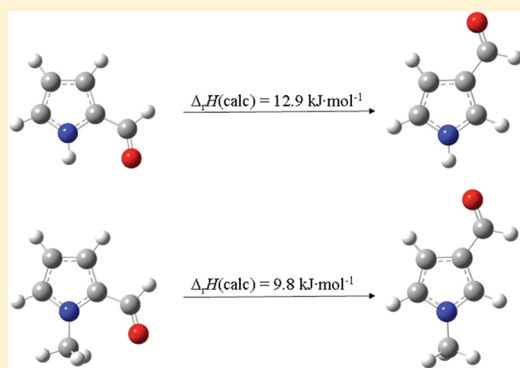
1. INTRODUCTION

Pyrrole is the building block of the naturally occurring porphyrins, the tetrapyrrolic "pigments of life", which include the organic component of the prosthetic group of blood, the hemoglobin heme, the green pigment of leaves, chlorophyll, vitamin B[12], and the bile pigments.[1,2] The aldehyde derivative, 2-pyrrolecarboxaldehyde, studied in this work, is used in the synthesis of porphyrins with unsubstituted meso positions.[3] It has biological and industrial applications, and it is widely used as added compound to tobacco to enhance the flavor.

Several pyrrole derivatives have also been reported in various processed foods and beverages,[4−6] and because of their organoleptic properties, some of them are used as flavor additives.[7] 2-Pyrrolecarboxaldehyde and 1-methyl-2-pyrrole-carboxaldehyde contributed to the roasted meat flavor,[8] and they have been identified in popcorn,[4] potato chips,[9] raw and roasted cocoa,[10] and in coffee, showing a great antioxidant activity.[11−13]

2-Pyrrolecarboxaldehyde has been subject of several studies, both in the gas phase and in solution. In 1974, Marstokk and Møllendal, by microwave spectroscopy, showed that the stable form of this molecule is planar with the N—H and C=O bonds in a syn conformation.[14] A weak intramolecular hydrogen bond

between the carbonyl oxygen and the H atom from the N—H bond may be a cause of such orientation of the molecule in the gas phase.

John and collaborators carried out, in 1977, several calculations, using the ab initio molecular orbital theory with the minimal STO-3G basis set (HF/STO-3G on the present notation), to study the conformational preferences of 2- and 3-pyrrolecarboxaldehydes. Although these are nowadays standard and rudimental calculations, it is interesting to register their conclusions. They determined that both isomers adopt a planar *syn* conformation; for 2-pyrrolecarboxaldehyde the *syn* conformation is 7.8 kJ·mol^{-1} more stable than the *anti* one, and the existence of an intramolecular hydrogen bond is considered. For the 3-isomer, the *syn* orientation is only 1.6 kJ·mol^{-1} more favorable than the *anti* one.[15] However, other studies of the 3-pyrrolecarboxaldehyde have established that the *anti* conformer is preferred in solution.[15] Some studies of 2-pyrrolecarboxaldehyde in solution revealed that the molecule also adopts the conformation where the N—H and the C=O groups are in *syn* orientation.[16−18]

The infrared study in solution, due to Kaye et al., also reported that the 1-methyl derivative has a preference for the *syn* conformation.[17] Their study showed a different behavior of the C=O group after the introduction of the methyl group in the first position of pyrrole ring, i.e., the wavenumber of the absorption band increased by the replacement of N—H by N—CH₃ instead of decreasing (typical behavior due to the inductive effect of the −CH₃ group), which is explained by the removal of the weak intramolecular hydrogen bond interaction in 2-pyrrolecarboxaldehyde when the methyl group is introduced. However, Dubis and Grabowski, through a topological analysis based on the Bader theory, showed that this hydrogen bond does not exist in 2-pyrrolecarboxaldehyde, but a C—H⋯O intramolecular hydrogen bond was found for the *N*-methyl derivative, even if for a transition state.[18] These researchers also carried out a computational study of 2-pyrrolecarboxaldehyde and 1-methyl-2-pyrrolecarboxaldehyde, at the B3LYP/6-311++G(d,p) level of theory, having determined their molecular structure and geometrical parameters; this study revealed that the *syn* conformers are more stable than the *anti* conformers, which is in agreement with the experimental infrared study performed by them in the same work.

Rice et al. published, in 2007, a combined supersonic jet infrared and computational approach, and they concluded that 2-pyrrolecarboxaldehyde adopts a *syn* conformation in the gas-phase. The MP2/6-311+G (2d,p) calculated results predict that, energetically, the *syn* conformer is 16.6 kJ·mol⁻¹ more favorable than the *anti*.[19] The same conclusion related to the preferred conformation of 2-pyrrolecarboxaldehyde was obtained by Kumar and collaborators, through UV−VIS and infrared spectroscopy as well as computational methods.[20] Experimental and computational data revealed the existence of an intramolecular hydrogen bond between the N—H and the C=O of the formyl group.

More recently, Giuliano et al. performed a study of the molecular structures of the two conformers of 2-pyrrolecarboxaldehyde, their vibrational spectra and the UV-induced photochemistry, by combining the method of low-temperature matrix isolation with infrared spectroscopy and also using quantum chemical calculations performed at both the DFT and MP2 levels of theory.[21] It was found that the *syn* form is more stable than the *anti* by ca. 15 kJ·mol⁻¹.

Because of their applications and properties, the understanding of the molecular and energetic properties of this kind of compound as well as their stability and reactivity has great importance, so the knowledge of their energetics−structure relationships is important. To establish these relationships the thermochemical parameters, mainly enthalpies of formation and bond dissociation enthalpies, are of great importance. These thermochemical parameters are fundamental to several fields ranging from chemistry, medicine, pharmaceutical sciences, biology, environmental and industrial chemistry to calculate the amount of energy involved in chemical reactions and other thermodynamic functions as well as to evaluate the stability of the molecules.

The only experimental thermochemical data available in the literature for the compounds under study in this paper is the standard molar enthalpy of formation in the condensed phase of 2-pyrrolecarboxaldehyde, measured in 1933 by Stern and Klebs.[22] This is an old measurement from a study that did not conform with the necessary requirements to the
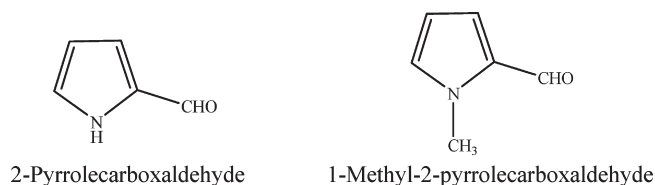

Figure 1. Structural formula of 2-pyrrolecarboxaldehyde and 1-methyl-2-pyrrolecarboxaldehyde.

determination of reliable values of standard molar enthalpies of formation so it was recalculated later in Cox and Pilcher compilation,[23] within the limitations of the few data that was available in the original paper.

This paper reports the experimental and computational determination of the standard ($p° = 0.1$ MPa) molar enthalpies of formation, in the gaseous phase, at $T = 298.15$ K, of 2-pyrrolecarboxaldehyde and 1-methyl-2-pyrrolecarboxaldehyde (Figure 1), following the same line of investigation performed for other pyrrole derivatives, already available in the literature.[24−32]

The standard molar enthalpies of formation, in the condensed phase, of both compounds, were obtained by static bomb combustion calorimetry, and their standard molar enthalpies of phase transition were determined by high-temperature Calvet microcalorimetry.

High-level ab initio molecular orbital calculations at the G3(MP2)//B3LYP level were carried out and the estimated gas-phase standard molar enthalpies of formation of 2-pyrrolecarboxaldehyde and 1-methyl-2-pyrrolecarboxaldehyde were obtained. These calculations were further extended to the 3-pyrrolecarboxaldehyde and 1-methyl-3-pyrrolecarboxaldehyde that were not studied experimentally.

2. EXPERIMENTAL SECTION

2.1. Materials and Purity Control. 2-Pyrrolecarboxaldehyde [CAS 1003−29−8] and 1-methyl-2-pyrrolecarboxaldehyde [CAS 1192−58−1] were obtained commercially from Sigma-Aldrich Chemical Co. and Alfa-Aesar, respectively, with a minimum molar fraction purity of 0.98.

The crystalline 2-pyrrolecarboxaldehyde was purified by repeated vacuum sublimations, and the liquid 1-methyl-2-pyrrolecarboxaldehyde was purified by successive fractional distillations under reduced pressure. Control of the purity was made by gas−liquid chromatography and also 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-pyrrolecarboxaldehyde (0.9995 ± 0.0004) and 1-methyl-2-pyrrolecarboxaldehyde (1.0006 ± 0.0002).

The literature values of the specific densities used were $\rho = 1.391$ g·cm⁻³ for 2-pyrrolecarboxaldehyde[33] and $\rho = 1.074$ g·cm⁻³ for 1-methyl-2-pyrrolecarboxaldehyde,[34] and the relative atomic masses used for the elements were the ones recommended by the IUPAC Commission in 2009.[35]

2.2. Combustion Calorimetry. All the combustion experiments were carried out in an isoperibol calorimetric system, equipped with a stainless steel twin valve bomb (Parr 1108 model), with an internal volume of 0.342 dm³. Both the apparatus and the operating technique have been previously described.[26,36−38]

12550

dx.doi.org/10.1021/jp2068057 |*J. Phys. Chem. B* 2011, 115, 12549–12557

The calorimetric system was calibrated following the procedure of Coops et al.,[39] with benzoic acid NIST Standard Reference Material, sample 39j;[40] the energy equivalent of the calorimeter was found to be $\varepsilon(\text{calor}) = 15995.3 \pm 2.0\ \text{J}\cdot\text{K}^{-1}$ (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 crystalline samples of benzoic acid and of 2-pyrrolecarboxaldehyde were burnt in pellet form, while the liquid 1-methyl-2-pyrrolecarboxaldehyde was ignited and contained in previously weighed polyester bags made of Melinex, 0.025 mm of thickness $[\Delta_c u^\circ(\text{Melinex}) = -22902 \pm 5\ \text{J}\cdot\text{g}^{-1}]$.[41]

The energetic effect for the amount of nitric acid produced in the combustion has been done as in previous studies.[24,25]

The amount of compound, $m(\text{cpd})$, 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 1-methyl-2-pyrrolecarboxaldehyde).

The corrections to the standard state, ΔU_Σ, and the calculation of the standard massic energies of combustion of both compounds, $\Delta_c u^\circ$, were made following the procedure given by Hubbard et al.[42]

2.3. High-Temperature Calvet Microcalorimetry. A high temperature Calvet microcalorimeter (Setaram HT 1000) was used, in this work, to measure the standard molar enthalpies of phase transition of the two studied compounds, through the drop microcalorimetric technique for vacuum sublimation, described by Skinner et al.,[43] for the sublimation of solid compounds and adapted, in our laboratory, for liquid vaporizations.[44] The measuring procedure and a detailed description have been previously described.[45]

The microcalorimeter was calibrated making use of the standard molar enthalpy of sublimation of naphthalene (Aldrich, mass fraction purity >0.99), $\Delta_{cr}^{g} H_m^\circ = 72.6 \pm 0.6\ \text{kJ}\cdot\text{mol}^{-1}$,[46] and of vaporization of n-undecane (Aldrich, mass fraction purity >0.99), $\Delta_l^g H_m^\circ (298.15\ \text{K}) = 56.580 \pm 0.566\ \text{kJ}\cdot\text{mol}^{-1}$.[46]

The calibration constants, k, of the calorimeter were obtained as the average of six independent experiments for the predefined temperatures, $k(T = 324\ \text{K}) = 1.0165 \pm 0.0012$ for the sublimation experiments of 2-pyrrolecarboxaldehyde and $k(T = 334\ \text{K}) = 1.0314 \pm 0.0030$ for the vaporization experiments of 1-methyl-2-pyrrolecarboxaldehyde; the uncertainties presented are the standard deviations of the mean.

3. COMPUTATIONAL DETAILS

Standard ab initio molecular orbital calculations[47] were performed with the Gaussian 03 computer code,[48] and the composite G3(MP2)//B3LYP approach was the methodology employed to compute the gas-phase enthalpies of all species considered.[49]

The absolute enthalpies, obtained at $T = 298.15\ \text{K}$, were used to estimate the enthalpy of formation of the compounds studied experimentally, by combining the enthalpy of the gas-phase working reactions 1−7 and the experimental enthalpies of formation of the molecules there included. The calculations were also extended to 3-pyrrolecarboxaldehyde and 1-methyl-3-

pyrrolecarboxaldehyde, molecules that were not studied experimentally.

$$(1)$$

$$(2)$$

$$(3)$$

$$(4)$$

$$(5)$$

$$(6)$$

$$(7)$$
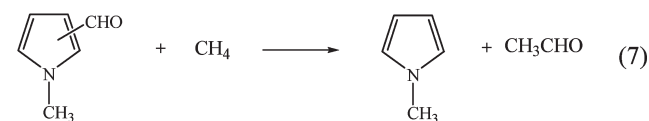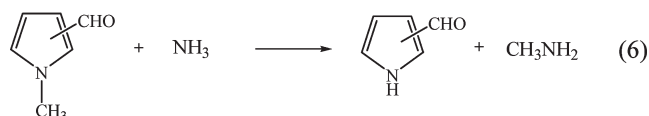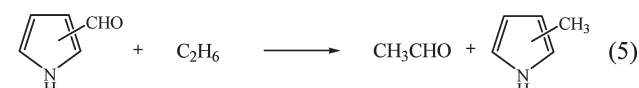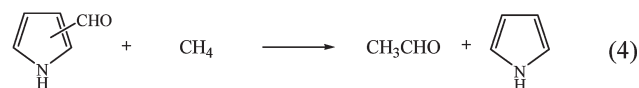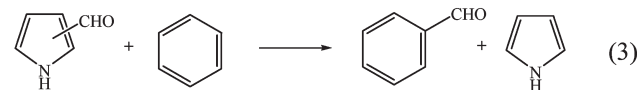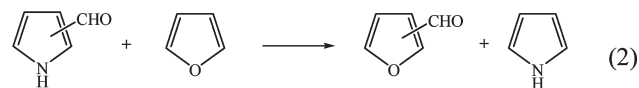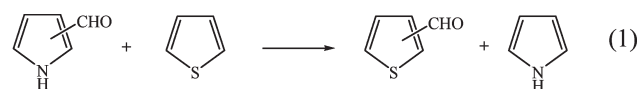
The same computational approach was also used to calculate the N−H bond dissociation enthalpies, gas-phase acidities and basicities, proton and electron affinities and adiabatic ionization enthalpies of all compounds considered.

4. RESULTS AND DISCUSSION

4.1. Condensed Phase and Phase Transition. Detailed results of one typical combustion experiment performed for 2-pyrrolecarboxaldehyde and 1-methyl-2-pyrrolecarboxaldehyde are presented in Table 1, in which $\Delta m(H_2O)$ represents the deviation of the mass of water added to the calorimeter from 3119.6 g, the mass assigned to $\varepsilon(\text{calor})$. The values of the energy associated to the isothermal bomb process, $\Delta U(\text{IBP})$, were calculated from eq 8

$$\Delta U(\text{IBP}) = -\{\varepsilon(\text{calor}) + c_p(H_2O, l)\Delta m(H_2O) + \varepsilon_f\}\Delta T_{ad}$$

$$+ \Delta U(\text{ign}) \qquad (8)$$

where ΔT_{ad} is the calorimeter temperature change corrected for the heat exchange and the work of stirring and the remaining terms are as previously defined.[42,50] Detailed data of each combustion experiment, for the compounds studied, are given in Tables S1 and S2 of Supporting Information.
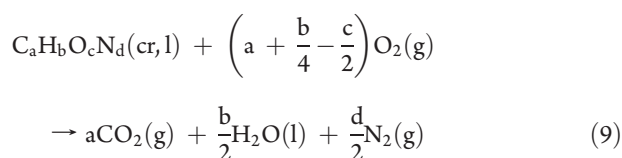
The individual values of $\Delta_c u^\circ$, together with the respective mean values, $\langle\Delta_c u^\circ\rangle$, and their standard deviations are presented in Table 2.

Table 1. Typical Combustion Results, at T = 298.15 K, ($p°$ = 0.1 MPa), for the Studied Compounds[a]

	2-pyrrole carboxaldehyde	1-methyl-2-pyrrolecarboxaldehyde
$m(CO_2$, total$)$/g	1.55570	1.59810
$m(cpd)$/g	0.66985	0.62071
$m'(fuse)$/g	0.00356	0.00311
$m''(Melinex)$/g		0.03979
ΔT_{ad}/K	1.13868	1.22376
ε_f/J·K^{-1}	15.51	15.75
$\Delta m(H_2O)$/g	0	−0.1
$-\Delta U(IBP)$ [b]/J	18230.50	19592.56
$\Delta U(fuse)$/J	57.81	50.51
$\Delta U(Melinex)$/J		911.28
$\Delta U(HNO_3)$/J	44.43	36.92
$\Delta U(ign)$/J	0.69	0.61
ΔU_Σ/J	13.28	12.51
$-\Delta_c u°$/J·g^{-1}	27043.34	29935.62

[a] $m(CO_2$, total) is the mass of CO_2 recovered in each combustion; $m(cpd)$ is the mass of compound burnt in each experiment; $m'(fuse)$ is the mass of the fuse (cotton) used in each experiment; $m''(Melinex)$ is the mass of Melinex used in each experiment; ΔT_{ad} is the corrected temperature rise; ε_f is the energy equivalent of the contents in the final state; $\Delta m(H_2O)$ is the deviation of mass of water added to the calorimeter from 3119.6 g; $\Delta U(IBP)$ is the energy change for the isothermal combustion reaction under actual bomb conditions and includes $\Delta U(ignition)$; $\Delta U(fuse)$ is the energy of combustion of the fuse (cotton); $\Delta U(Melinex)$ is the energy of combustion of the Melinex; $\Delta U(HNO_3)$ is the energy correction for the nitric acid formation; $\Delta U(ign)$ is the electric energy for the ignition; ΔU_Σ is the standard state correction; $\Delta_c u°$ is the standard massic energy of combustion. [b] ΔU-(IBP) includes $\Delta U(ignition)$.

The values of $\Delta_c u°$ refer to the general combustion reaction, described by the following equation

$$C_aH_bO_cN_d(cr,l) + \left(a + \frac{b}{4} - \frac{c}{2}\right)O_2(g)$$

$$\rightarrow aCO_2(g) + \frac{b}{2}H_2O(l) + \frac{d}{2}N_2(g) \qquad (9)$$

The derived standard molar energies, $\Delta_c U_m°(cr,l)$, and enthalpies, $\Delta_c H_m°(cr,l)$, of combustion and the standard molar enthalpies of formation, $\Delta_f H_m°(cr,l)$, in the condensed phase, at T = 298.15 K, for each compound are given in Table 3.

The uncertainties of the standard molar energy and enthalpy of combustion correspond to twice the overall standard deviation of the mean and include the contribution from the calibration with benzoic acid and from the values of the auxiliary quantities used.[51,52]

The values of the $\Delta_f H_m°(cr,l)$ at T = 298.15 K were derived from the $\Delta_c H_m°(cr,l)$, using the values of $\Delta_f H_m°$ of $H_2O(l)$, −285.830 ± 0.042 kJ·mol^{-1}, and $CO_2(g)$, −393.51 ± 0.13 kJ·mol^{-1}.[53]

Results of the measurements of the enthalpies of sublimation, or vaporization, for the compounds studied, obtained by Calvet microcalorimetry are given in Table 4. The observed enthalpies of phase transition, $\Delta_{cr,l}^{g,T}H_m°$, were corrected to

Table 2. Individual Values of Standard ($p°$ = 0.1 MPa) Massic Energies of Combustion, $\Delta_c u°$, of the Compounds at T = 298.15 K

2-pyrrolecarboxaldehyde	1-methyl-2-pyrrolecarboxaldehyde
$-\Delta_c u°$/J·g^{-1}	
27043.34	29938.48
27029.96	29935.62
27032.93	29923.54
27047.12	29935.15
27045.51	29948.64
27048.63	29946.67
	29924.60
$-\langle\Delta_c u°\rangle$/(J·g^{-1})	
(27041.2 ± 3.2)[a]	(29936.1 ± 3.7)[a]

[a] Mean value and standard deviation of the mean.

T = 298.15 K, $\Delta_{cr,l}^g H_m°$, through the eq 10, using the corrective term $\Delta_{298.15\ K}^T H_m°(g)$

$$\Delta_{298.15K}^T H_m°(g) = \int_{298.15K}^T C_{p,m}°(g)dT \qquad (10)$$

where T is the temperature of the hot reaction cells and $C_{p,m}°(g)$ is the gas-phase molar heat capacity of the compounds, derived from statistical thermodynamics using the vibrational frequencies from DFT calculations, B3LYP/6-31G(d) approach (scaled by 0.9614).[54] The $C_{p,m}°(g)$ = f(T) obtained for 2-pyrrolecarboxaldehyde and for 1-methyl-2-pyrrolecarboxaldehyde are represented by eqs 11 and 12, respectively.

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

$$C_{p,m}°(g)(J·K^{-1}·mol^{-1}) = -4.84338\times10^{-7}(T/K)^3$$
$$+4.00446 \times 10^{-4}(T/K)^2$$
$$+1.83256 \times 10^{-1}(T/K)$$
$$+21.748\ (R^2 = 0.99987) \qquad (11)$$

$$C_{p,m}°(g)/(J·K^{-1}·mol^{-1}) = -5.22684\times10^{-7}(T/K)^3$$
$$+4.58306 \times 10^{-4}(T/K)^2$$
$$+2.06411 \times 10^{-1}(T/K)$$
$$+34.094\ (R^2 = 0.99995) \qquad (12)$$

The gas-phase molar heat capacities for 2-pyrrolecarboxaldehyde and 1-methyl-2-pyrrolecarboxaldehyde, between 150 and 600 K, are listed in Table S3 of Supporting Information.

Table 5 summarizes the experimental derived standard molar enthalpies of formation in the gas phase, $\Delta_f H_m°(g)$, at T = 298.15 K, for the two studied compounds.

4.2. Gas-Phase Molecular Structures. The calculated most stable conformations of 2-pyrrolecarboxaldehyde, 3-pyrrolecarboxaldehyde, 1-methyl-2-pyrrolecarboxaldehyde, and 1-methyl-3-pyrrolecarboxaldehyde, optimized at the B3LYP/6-31G(d) level of theory [(G3(MP2)//B3LYP calculations] are those represented in Figure 2. Selected bond lengths and bond angles are also included.

Table 3. Derived Standard (p° = 0.1 MPa) Molar Energies of Combustion, $\Delta_c U^\circ_m$, Standard Molar Enthalpies of Combustion, $\Delta_c H^\circ_m$, and Standard Molar Enthalpies of Formation, $\Delta_f H^\circ_m$, for the Compounds Studied at T = 298.15 K

compound	$-\Delta_c U^\circ_m(cr,l)/(kJ \cdot mol^{-1})$	$-\Delta_c H^\circ_m(cr,l)/(kJ \cdot mol^{-1})$	$-\Delta_f H^\circ_m(cr,l)/(kJ \cdot mol^{-1})$
2-pyrrolecarboxaldehyde (cr)	2571.6 ± 1.1	2572.2 ± 1.1	109.9 ± 1.2
1-methyl-2-pyrrolecarboxaldehyde (l)	3266.8 ± 1.5	3268.7 ± 1.5	92.8 ± 1.7

Table 4. Standard (p° = 0.1 MPa) Molar Enthalpies of Phase Transition, $\Delta^g_{cr,l} H^\circ_m$, for the Two Compounds, at T = 298.15 K, Determined by Calvet Microcalorimetry

compound	no. experiments	T/K	$\Delta^{g,T}_{cr,l,298.15\ K} H^\circ_m/(kJ \cdot mol^{-1})$	$\Delta^T_{298.15K} H^\circ_m(g)/(kJ \cdot mol^{-1})$	$\Delta^g_{cr,l} H^\circ_m(298.15K)/(kJ \cdot mol^{-1})$
2-pyrrolecarboxaldehyde (cr)	5	324.3	81.3 ± 0.2	2.6926 ± 0.0015	78.6 ± 1.3
1-methyl-2-pyrrolecarboxaldehyde (l)	5	334.3	60.5 ± 0.1	4.6512 ± 0.0007	55.8 ± 1.2

Table 5. Comparison Between the Experimental and Computed G3(MP2)//B3LYP Gas-Phase Enthalpies of Formation of the Pyrrolecarboxaldehyde Isomers and Derivatives at T = 298.15 K ^{a}

	$-\Delta_f H^\circ_m(g)/(kJ \cdot mol^{-1})$				
reaction	2-pyrrolecarboxaldehyde	3-pyrrolecarboxaldehyde	reaction	1-methyl-2-pyrrolecarboxaldehyde	1-methyl-3-pyrrolecarboxaldehyde
1	30.9 (−0.4)	20.8	6	38.5 (1.5)	28.6
2	25.8 (−5.5)	16.8	7	36.1 (−0.9)	26.6
3	29.7 (−1.6)	17.2	atom.	35.9 (−1.1)	26.4
4	31.7 (0.4)	19.2			
5	30.2 (−1.1)	17.7			
atom.	31.1 (−0.2)	18.6			
Exp.	31.3 ± 1.8			37.0 ± 2.1	

^{a} Enthalpic differences between the experimental and computed values are given in parentheses.

At this level of theory, the four molecules adopt a planar structure. The N—H,O-*syn* is the most stable conformation adopted by 2-pyrrolecarboxaldehyde and 1-methyl-2-pyrrolecarboxaldehyde, which is in agreement with the studies in solution and in the gas phase cited in the Introduction as well as with the analogues 2-acetylpyrrole,[24] 1-methyl-2-acetylpyrrole,[26] 2-pyrrolecarboxylic acid,[25] and 1-methyl-2-pyrrolecarboxylic acid;[25] the N—H,O-*anti* conformation is 14.8 and 14.6 kJ·mol^{-1} less stable than the N—H,O-*syn*, for 2-pyrrolecarboxaldehyde and 1-methyl-2-pyrrolecarboxaldehyde, respectively, which is in accordance with the enthalpic differences found by Dubis,[18] Rice,[19] and Giuliano.[21]

In 2-pyrrolecarboxaldehyde, the C_5NH angle is ca. 8° larger that the C_2NH (128.0 vs 120.2°, respectively), suggesting that the pyrrole N—H hydrogen atom is slightly moved in the direction of the carbonyl oxygen atom, which was already found for 2-acetylpyrrole,[24] 2-pyrrolecarboxylic acid,[25] 2-trichloroacetylpyrrole,[29] and 2-trifluoroacetylpyrrole.[29] A weak intramolecular hydrogen bond between the C=O and N—H groups may be a cause of this orientation of the molecule in the gas phase. To confirm the existence of such interaction, a topological analysis with the Topmod program was performed aiming at the location of critical points in the electronic charge density distribution in the region between the H and O atoms.[55] This analysis revealed a bond critical point in 2-pyrrolecarboxaldehyde in the referred region: the values of electron density in the critical point are η = 0.031 (electron localization function), ρ = 0.0074 (electron density), and $\nabla^2\rho$ = 0.0218 (Laplacian of the electron density), calculated at the B3LYP/6-311+G(2d,2p) level of theory. This result is in agreement with the experimental and computational

studies already cited in the Introduction as well as with the pyrrole derivatives cited above, except with the topological analysis carried out by Dubis and Grabowski, in which this hydrogen bond does not exist in 2-pyrrolecarboxaldehyde.

The NC_2C_6 angle increases by the replacement of the H atom in the N—H group of 2-pyrrolecarboxaldehyde by a —CH$_3$ group to form the 1-methyl-2-pyrrolecarboxaldehyde (120.2 vs 124.5°, respectively), which is explained by the removal of the weak intramolecular hydrogen bond interaction in 2-pyrrolecarboxaldehyde when the methyl group is introduced.

Moreover, the O···H distance (0.2574 nm) in 2-pyrrolecarboxaldehyde is at the order of hydrogen bond length, which agrees well with the corresponding one obtained by Marstokk[14] and Kumar[20] but is slightly lower (~0.006 nm) than the value found by Dubis and Grabowski.[18]

For 3-pyrrolecarboxaldehyde, the N—H,O-*anti* conformation is slightly more stable than the *syn* structure, by only 1.0 kJ·mol^{-1}. The computational studies due to John and collaborators revealed the opposite, i.e., the *syn* orientation is 1.6 kJ·mol^{-1} more favorable than the *anti*.[15] The N—H,O-*syn* conformation is also preferred by the 3-acetyl analogue, only by 0.8 kJ·mol^{-1}.[24] In what concerns the 1-methyl-3-pyrrolecarboxaldehyde, this molecule also adopts a N—H,O-*anti* orientation, which is only 0.4 kJ·mol^{-1} more favorable than the *syn* conformation, but once more is opposite to the result obtained for the 1-methyl-3-acetylpyrrole (*syn* conformation is 1.2 kJ·mol^{-1} more stable than the *anti*).[26]

In a general way, there are not significant differences between the geometrical parameters obtained in this work for the four molecules studied and the corresponding ones found in the
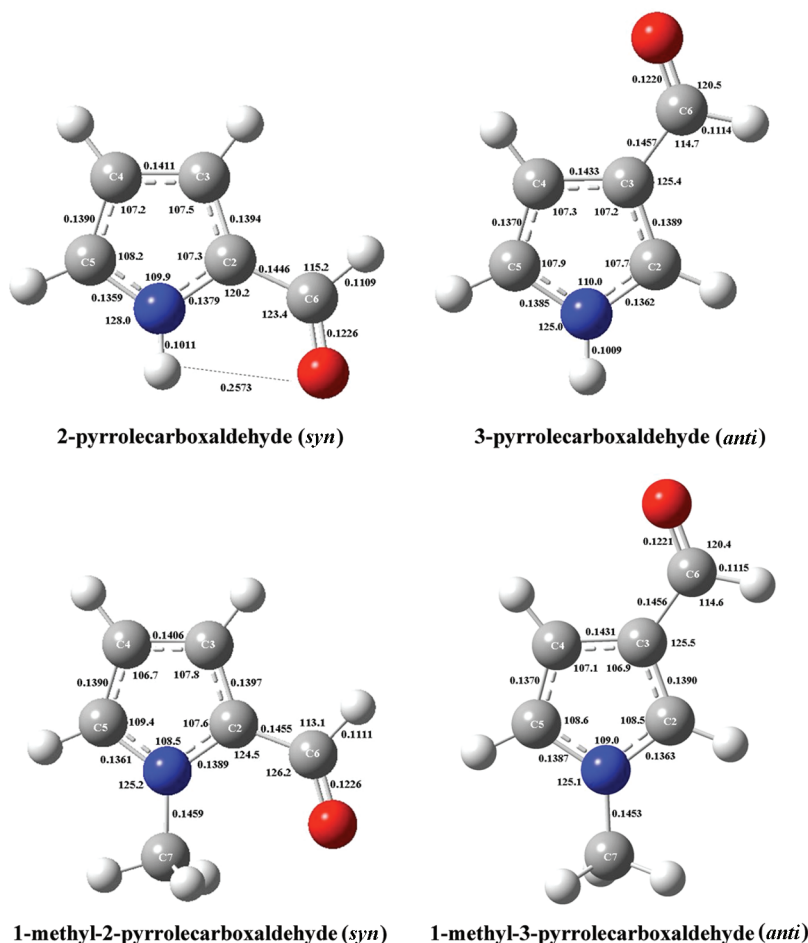
12553

dx.doi.org/10.1021/jp2068057 |*J. Phys. Chem. B* 2011, 115, 12549–12557

Figure 2. B3LYP/6-31G(d) optimized most stable configurations for 2-pyrrolecarboxaldehyde (*syn*), 3-pyrrolecarboxaldehyde (*anti*), 1-methyl-2-pyrrolecarboxaldehyde (*syn*), and 1-methyl-3-pyrrolecarboxaldehyde (*anti*). Selected bond lengths (nm) and bond angles (degrees) are included.

literature, cited in the Introduction, and for the analogues pyrrole derivatives.

4.3. Gas-Phase Experimental and Theoretical Enthalpies of Formation. For 2-pyrrolecarboxaldehyde, there is in the literature a value for its standard molar enthalpy of formation, in the crystalline phase, determined in 1933, by Stern and Klebs as -106.4 ± 2.5 kJ·mol^{-1} (value reanalyzed by Cox and Pilcher,[23] original value -102 kJ·mol^{-1},[22]), which differs from our value (Table 3) by 3.5 kJ·mol^{-1}. The Pedley compendium also reported this reanalyzed value in the crystalline phase: -106.4 ± 2.5 kJ·mol^{-1}.[56] No experimental or computational data for the other compounds studied have been found in the literature to compare with our results.

The gas-phase standard molar enthalpies of formation of 2-pyrrolecarboxaldehyde and of 1-methyl-2-pyrrolecarboxaldehyde were estimated by combining the enthalpy of reactions 1−5 and 6 and 7, respectively, computed at the G3(MP2)//B3LYP level with the experimental enthalpies of formation of the auxiliary molecules used. Their enthalpies of formation have also been estimated from the computed enthalpy of atomization reaction, at $T = 298.15$ K, obtained by the same computational approach, and are reported in Table 5. All the experimental values of $\Delta_f H_m^\circ$(g) of the auxiliary species used in the working reactions are presented in Table S4 of the Supporting Information.

For 2-pyrrolecarboxaldehyde, the estimated values almost match the experimental one; the best estimate is obtained when

the atomization reaction is considered, with an enthalpic difference of only 0.2 kJ·mol^{-1}. It is important to note that the deviations obtained are smaller than the uncertainty associated with the experimental value, except when eq 2 is used, for which a larger difference is obtained (5.5 kJ·mol^{-1}).

The estimates based on the working reactions 6 and 7 as well as the atomization reaction for 1-methyl-2-pyrrolecarboxaldehyde almost fit the experimental result, with all deviations falling within the experimental uncertainty. The experimental value of $\Delta_f H_m^\circ$(g) of 2-pyrrolecarboxaldehyde obtained in this work was used in the working reaction 6 to estimate $\Delta_f H_m^\circ$(g) of 1-methyl-2-pyrrolecarboxaldehyde, leading to a calculated value that only differs by 1.5 kJ·mol^{-1} from the experimental one, which strongly supports our results. It is worth noticing that the calculated values by the G3(MP2)//B3LYP have an average absolute deviation as large as 5.2 kJ·mol^{-1}.[49] Despite the average absolute deviation of the values calculated by the G3(MP2)//B3LYP, the data obtained by using the different working reactions (Table 5) are among them and, with the experimental result, well within this possible deviation.

Because of the excellent agreement obtained between the experimental and calculated data for 2-pyrrolecarboxaldehyde and 1-methyl-2-pyrrolecarboxaldehyde, the G3(MP2)//B3LYP computations were also extended to the estimation of the $\Delta_f H_m^\circ$(g) of the 3-isomers, namely, 3-pyrrolecarboxaldehyde

12554

dx.doi.org/10.1021/jp2068057 |*J. Phys. Chem. B* 2011, 115, 12549–12557

Table 6. G3(MP2)//B3LYP Computed Bond Dissociation Enthalpies, N—H BDE, Gas-Phase Acidities, $\Delta G_{acidity}$, and Basicities, $\Delta G_{basicity}$, Proton Affinities, PA, at $T = 298.15$ K and Electron Affinities, EA, and Adiabatic Ionization Enthalpies, IE, at $T = 0$ K, for the Compounds Studied (All Values in kJ·mol^{-1})

compound	N—H BDE	$\Delta G_{acidity}$	$\Delta G_{basicity}$	PA	EA	IE
2-pyrrolecarboxaldehyde	412.3	1409.5	843.2	874.9 (O)	−7.7	840.3
3-pyrrolecarboxaldehyde	405.6	1399.2	852.5	885.0 (O)	−44.1	835.5
1-methyl-2-pyrrolecarboxaldehyde			859.2	891.9 (O)	−10.8	820.2
1-methyl-3-pyrrolecarboxaldehyde			870.3	904.8 (O)	−38.0	812.2

(working reactions 1—5) and 1-methyl-3-pyrrolecarboxaldehyde (working reactions 6 and 7). The results obtained for these two last molecules are also given in Table 5, and for each one, different reactions lead to similar gas-phase enthalpies of formation, which allowed us to define a mean value for the $\Delta_f H_m^\circ$ (g) of 3-pyrrolecarboxaldehyde and 1-methyl-3-pyrrolecarboxaldehyde, as −18.4 kJ·mol^{-1} and −27.2 kJ·mol^{-1}, respectively.

The computed G3(MP2)//B3LYP enthalpies for the compounds studied, auxiliary molecules, and atoms used in the working reactions 1—7 are presented in Table S4 in the Supporting Information.

4.4. Other Gas-Phase Thermodynamic Properties. Other thermodynamic properties for all the pyrrolecarboxaldehydes considered were calculated in this work by extending the G3-(MP2)//B3LYP computations to their radicalar, cationic, and anionic species. The entire set of results obtained are presented in Table 6: bond dissociation enthalpies, N—H BDE, gas-phase acidities, $\Delta G_{acidity}$, and basicities, $\Delta G_{basicity}$, proton affinities, PA at $T = 298.15$ K, as well as electron affinities, EA, and adiabatic ionization enthalpies, IE, at $T = 0$ K.

Thermodynamic data for these two compounds is scarce in the literature; only the gas-phase ionization enthalpy (IE) for 2-pyrrolecarboxaldehyde, measured by Linda and Marino, using an electron impact technique was found in the literature as 861.6 ± 4.8 kJ·mol^{-1}.[57] The experimental value obtained by them differs by 21.3 kJ·mol^{-1} from the result computed in this work. Similar enthalpic differences between the experimental and calculated data obtained with the same G3(MP2)//B3LYP approach were found for 2- and 3-fluoroanilines,[58] for 2-acetylpyrrole,[24] and for 2-trifluoroacetylpyrrole.[29] Regarding the values of IE presented in Table 6, the energy required to remove an electron is higher when the —CHO group is in the second position of the ring toward the third position. The entrance of a methyl group in the first position of 2- and 3-pyrrolecarboxaldehydes increases their capacity of acting as an electron-donor species by ca. 20 kJ·mol^{-1}. The values of IE follow the trend 2-pyrrolecarboxaldehyde >2-pyrrolecarboxylic acid[25] > 2-acetylpyrrole[24] as well as in the corresponding methyl derivatives.[25,26]

The computed N—H BDE for 2-pyrrolecarboxaldehyde is 6.7 kJ·mol^{-1} higher than for the 3-isomer, which also supports the existence of an interaction of type N—H···O, already referred in the section 4.2. The knowledge of the energy required for the N—H bonds cleavage is important to evaluate the antioxidant strength of compounds with this type of bond. The lower the N—H BDE is, the higher the antioxidant activity. Thus, if we consider just the N—H BDE values, we can state that 2-pyrrolecarboxaldehyde and 2-acetylpyrrole have similar antioxidant properties (N—H BDE = 412.3 and 408.3 kJ·mol^{-1},[24] respectively) and that they are more effective antioxidants than 2-pyrrolecarboxylic acid (N—H BDE = 421.6 kJ·mol^{-1}).[25]

The calculated $\Delta G_{acidity}$ values presented in Table 6 indicate that the removal of a proton in 3-pyrrolecarboxaldehyde is easier by ca. 10 kJ·mol^{-1} than in the 2-isomer, following the same behavior of the acetylpyrroles analogues.[24] In what concerns the $\Delta G_{basicity}$ values, the 3-pyrrolecarboxaldehyde is more basic that the 2-isomer, which is also observed in the respective N-methyl derivatives. The basic character of the compounds increases from 2-pyrrolecarboxylic acid (813.2 kJ·mol^{-1})[25] < 2-pyrrolecarboxaldehyde (843.2 kJ·mol^{-1}) < 2-acetylpyrrole (858.5 kJ·mol^{-1}).[24]

All the pyrrolecarboxaldehydes studied in this work protonate, preferentially, on the carbonyl oxygen atom, which was already verified for the acetylpyrroles,[24,26] pyrrolecarboxylic acids,[25] and nitropyrroles (the preferred protonation site is in one of the oxygen atoms of the nitro group).[59] The N atom was found to be the least favorable protonation site for all the pyrrole derivatives cited. The values of PA presented in Table 6 show that O protonation occurs more easily in the 3-isomers than in the corresponding 2-derivatives; a similar behavior has already been reported for the acetylpyrroles.[24,26] When a methyl group is attached at the N position of 2- and 3-pyrrolecarboxaldehydes to yield the respective 1-methyl-2- and 1-methyl-3-pyrrolecarboxaldehydes, the proton affinity increases by 17.0 and 19.8 kJ·mol^{-1}, respectively.

All the computed proton affinity values of each protonation site for the four pyrrolecarboxaldehydes studied are collected in Table S5 in the Supporting Information.

The computed electron affinities presented in Table 6 show that the addition of one electron to 2-pyrrolecarboxaldehyde and their N-methyl derivative is easier than in the corresponding 3-isomers. This behavior was already observed in the acetylpyrroles and their N-methyl derivatives.[24,26]

5. CONCLUSIONS

The standard molar gas-phase enthalpies of formation, at $T = 298.15$ K, of 2-pyrrolecarboxaldehyde and 1-methyl-2-pyrrolecarboxaldehyde have been obtained through experimental and computational methods. Experimentally, static-bomb combustion calorimetry and high-temperature Calvet microcalorimetry have been used. Computational calculations at the G3(MP2)//B3LYP level have been carried out, and the estimated gas-phase enthalpies of formation of the two referred compounds compare very well with the experimental data. Thus, the computational calculations were extended to the 3-isomers, 3-pyrrolecarboxaldehyde and the 1-methyl-3-pyrrolecarboxaldehyde, and a mean computational $\Delta_f H_m^\circ$ (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. It was found that the N—H,O-syn is the most stable conformation adopted by 2-pyrrolecarboxaldehyde and 1-methyl-2-pyrrolecarboxaldehyde, while the N—H,O-$anti$ conformation is slightly more stable than

the *syn* structure for the respective 3-isomers. For 2-pyrrolecarboxaldehyde, a topological analysis has been carried out, and it revealed a bond critical point in the region between the H (from N—H) and O atoms, suggesting the existence of an interaction of type N—H···O, in agreement with the experimental and computational studies already cited in the Introduction as well as in previous studies reported for 2-acetylpyrrole, 2-pyrrolecarboxylic acid, 2-trichloroacetylpyrrole, and 2-trifluoroacetylpyrrole.

Other thermodynamic properties of the four referred compounds, namely, N—H bond dissociation enthalpies, gas-phase acidities and basicities, proton and electron affinities, and gas-phase adiabatic ionization enthalpies have also been obtained by means of G3(MP2)//B3LYP calculations.

■ ASSOCIATED CONTENT

ⓢ Supporting Information.   Detailed data of all the combustion calorimetric experiments for 2-pyrrolecarboxaldehyde and 1-methyl-2-pyrrolecarboxaldehyde, the computational gas-phase molar heat capacities for 2-pyrrolecarboxaldehyde and 1-methyl-2-pyrrolecarboxaldehyde, the G3(MP2)//B3LYP enthalpies (energies plus thermal corrections for T = 298.15 K) for 2-pyrrolecarboxaldehyde, 3-pyrrolecarboxaldehyde, 1-methyl-2-pyrrolecarboxaldehyde, 1-methyl-3-pyrrolecarboxaldehyde, and for the auxiliary molecules and atoms used in the several working reactions as well as the standard molar enthalpies of formation, at T = 298.15 K, taken from the literature, the G3(MP2)//B3LYP computed proton affinities, PA, at T = 298.15 K, for 2-pyrrolecarboxaldehyde, 3-pyrrolecarboxaldehyde, 1-methyl-2-pyrrolecarboxaldehyde, and 1-methyl-3-pyrrolecarboxaldehyde, are presented in the Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

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

■ ACKNOWLEDGMENT

■ REFERENCES

(1) Falk, H. *The Chemistry of Linear Oligopyrroles and Bile Pigments*; Springer: Berlin, 1989.
(2) Battersby, A. R. *Nat. Prod. Rep.* **2000**, *17*, 507–526.
(3) Wiehe, A.; Ryppa, C.; Senge, M. O. *Org. Lett.* **2002**, *4*, 3807–3809.
(4) Buttery, R. G.; Ling, L. C.; Ster, D. J. *J. Agric. Food Chem.* **1997**, *45*, 837–843.
(5) Fuster, M. D.; Mitchell, A. E.; Ochi, H.; Shibamoto, T. *J. Agric. Food Chem.* **2000**, *48*, 5600–5603.
(6) Mahajan, S. S.; Goddik, L.; Qian, M. C. *J. Dairy Sci.* **2004**, *87*, 4057–4063.
(7) Maga, J. A. *J. Agric. Food Chem.* **1981**, *29*, 691–694.
(8) Raes, K.; Balcaen, A.; Dirinck, P.; De Winne, A.; Claeys, E.; Demeyer, D.; De Smet, S. *Meat Sci.* **2003**, *65*, 1237–1246.

(9) Lojzova, L.; Riddellova, K.; Hajslova, J.; Zrostlikova, J.; Schurek, J.; Cajka, T. *Anal. Chim. Acta* **2009**, *641*, 101–109.
(10) Ziegleder, G. *Z. Lebensm. Unters. Forsch.* **1991**, *192*, 521–525.
(11) Yanagimoto, K.; Lee, K.-G.; Ocho, H.; Shibamoto, T. *J. Agric. Food Chem.* **2002**, *50*, 5480–5484.
(12) Yeretzian, C.; Jordan, A.; Lindinger, W. *Int. J. Mass Spectrom.* **2003**, *223−224*, 115–139.
(13) G.-Rios, O.; S.-Quiroz, M.; Boulanger, R.; Barel, M.; Guyot, B.; Guiraud, J.-P.; S.-Galindo, S. *J. Food Compos. Anal.* **2007**, *20*, 297–307.
(14) Marstokk, K. M.; Møllendal, A. H. *J. Mol. Struct.* **1974**, *23*, 93–101.
(15) John, I. G.; Ritchie, G. L. D.; Radom., L. *J. Chem. Soc. Perkin Trans. 2* **1977**, 1601–1607.
(16) Farnier, M.; Drakenberg, T. *J. Chem. Soc., Perkin Trans. 2* **1975**, 333–337.
(17) Kaye, P. T.; Macrae, R.; Meakins, G. D.; Patterson, C. H. *Chem. Soc., Perkin Trans. 2* **1980**, 1631–1635.
(18) Dubis, A. T.; Grabowski, S. J. *J. Phys. Chem. A* **2003**, *107*, 8723–8729.
(19) Rice, C. A.; Dauster, I.; Suhm, M. A. *J. Chem. Phys.* **2007**, *126*, 134313–134318.
(20) Kumar, N.; Chakravorti, S.; Chowdhury, P. *J. Mol. Struct.* **2008**, *891*, 351–356.
(21) Giuliano, B. M.; Reva, I.; Fausto, R. *J. Phys. Chem. A* **2010**, *114*, 2506–2517.
(22) Stern, A.; Klebs, G., *Ann. Chim.*, 1933, 505, 295−306., In NIST Chemistry Webbook, NIST Standard Reference Database Number 69; Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg MD, 20899, (http://webbook.nist.gov).
(23) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organo-metallic Compounds*; Academic Press: New York, 1970.
(24) Santos, A. F. L. O. M.; Gomes, J. R. B.; Ribeiro da Silva, M. A. V. *J. Phys. Chem. A* **2009**, *113*, 3630–3638.
(25) Santos, A. F. L. O. M.; Ribeiro da Silva, M. A. V. *J. Phys. Chem. A* **2009**, *113*, 9741–9750.
(26) Ribeiro da Silva, M. A. V.; Santos, A. F. L. O. M. *J. Phys. Chem. B* **2010**, *114*, 2846–2851.
(27) Santos, A. F. L. O. M.; Ribeiro da Silva, M. A. V. *J. Chem. Thermodyn.* **2010**, *42*, 734–741.
(28) Santos, A. F. L. O. M.; Ribeiro da Silva, M. A. V. *J. Chem. Thermodyn.* **2010**, *42*, 1016–1023.
(29) Santos, A. F. L. O. M.; Ribeiro da Silva, M. A. V. *J. Chem. Thermodyn.* **2010**, *42*, 1079–1086.
(30) Santos, A. F. L. O. M.; Ribeiro da Silva, M. A. V. *J. Chem. Thermodyn.* **2010**, *42*, 1441–1450.
(31) Ribeiro da Silva, M. A. V.; Santos, A. F. L. O. M. *J. Phys. Chem. B* **2010**, *114*, 16214–16222.
(32) Santos, A. F. L. O. M.; Ribeiro da Silva, M. A. V. *J. Chem. Thermodyn.* **2011**, *43*, 1480–1487.
(33) Yaws, C. L.; Chen, D. H. In *Thermophysical Properties of Chemicals and Hydrocarbons*; Yaws, C. L., Ed.; William Andrew Inc., 2008, Chapter 5.
(34) *Alfa Aesar Catalogue*, Germany 2008−2009.
(35) Wieser, M. E.; Coplen, T. B. *Pure Appl. Chem.* **2011**, *83*, 359–396.
(36) Ribeiro da Silva, M. A. V.; Ribeiro da Silva, M. D. M. C.; Pilcher, G. *Rev. Port. Quím.* **1984**, *26*, 163–172.
(37) Ribeiro da Silva, M. A. V.; Ribeiro da Silva, M. D. M. C.; Pilcher, G. *J. Chem. Thermodyn.* **1984**, *16*, 1149–1155.
(38) Matos, M. A. R.; Sousa, C. C. S.; Morais, V. M. F. *J. Chem. Thermodyn.* **2009**, *41*, 308–314.
(39) Coops, J.; Jessup, R. S.; van Nes, K. G. In *Experimental Thermochemistry*; Rossini, F. D., Ed.; Interscience: New York, 1956; Vol 1, Chapter 3.
(40) Certificate of Analysis, Standard Reference Material 39j Benzoic Acid Calorimetric Standard. NBS, WA, 1995.
(41) Skinner, H. A.; Snelson, A. *Trans. Faraday Soc.* **1960**, *56*, 1776–1783.

(42) Hubbard, W. N.; Scott, D. W.; Waddington, G. In *Experimental Thermochemistry*; Rossini, F. D., Ed.; Interscience: New York, 1956; Vol 1, Chapter 5.

(43) Adedeji, F. A.; Brown, D. L. S.; Connor, J. A.; Leung, M.; Paz-Andrade, M. I.; Skinner, H. A. *J. Organomet. Chem.* **1975**, *97*, 221–228.

(44) Ribeiro da Silva, M. A. V.; Matos, M. A. R.; Amaral, L. M. P. F. *J. Chem. Thermodyn.* **1995**, *27*, 565–574.

(45) Santos, L. M. N. B. F.; Schröder, B.; Fernandes, O. O. P.; Ribeiro da Silva, M. A. V. *Thermochim. Acta* **2004**, *415*, 15–20.

(46) Sabbah, R.; Xu-wu, A.; Chickos, J. S.; Leitão, M. L. P.; Roux, M. V.; Torres, L. A. *Thermochim. Acta* **1999**, *331*, 93–204.

(47) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(48) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

(49) Baboul, A. G.; Curtiss, L. A.; Redfern, P. C.; Raghavachari, K. *J. Chem. Phys.* **1999**, *110*, 7650–7657.

(50) Westrum, E. F. In *Combustion Calorimetry*; Sunner, S.; Månsson, M., Eds.; Pergamon: Oxford, 1979; Vol 1, Chapter 7.

(51) Rossini, F. D. In *Experimental Thermochemistry*; Rossini, F. D., Ed.; Interscience: New York, 1956; Vol 1, Chapter 14.

(52) Olofsson, G. In *Combustion Calorimetry*; Sunner, S.; Månsson, M., Eds.; Pergamon: Oxford, 1979; Vol 1, Chapter 6.

(53) *CODATA Key Values for Thermodynamics*; Cox, J. D.; Wagman, D. D.; Medvedev, V. A., Eds.; Hemisphere: New York, 1989.

(54) Irikura, K. K. *THERMO.PL*; National Institute of Standards and Technology, 2002.

(55) Noury, S.; Krokidis, X.; Fuster, F.; Silvi, B. *Comput. Chem.* **1999**, *23*, 597–604.

(56) Pedley, J. B. *Thermochemical Data and Structures of Organic Compounds*; Thermodynamics Research Centre: College Station, TX, 1994.

(57) Linda, P.; Marino, G.; Pignataro, S. *J. Chem. Soc. B* **1971**, 1585–1587.

(58) Ribeiro da Silva, M. A. V.; Ferreira, A. I. M. C. L.; Gomes, J. R. B. *J. Phys. Chem. B* **2007**, *111*, 2052–2061.

(59) Esseffar, M.; Quintanilla, E.; Dávalos, J. Z.; Abboud, J. L. M.; Mó, O.; Yáñez, M. *New J. Chem.* **2002**, *26*, 1567–1574.