Energetics and molecular structure of alkyl 1-methylpyrrolecarboxylates (alkyl = methyl or ethyl)

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A B S T R A C T

Calorimetric techniques, namely static bomb calorimetry and high temperature Calvet microcalorimetry were used to derive, respectively, the standard (p^o = 0.1 MPa) molar enthalpy of formation, in the liquid phase, $\Delta_f H_m^o$ (l), and the standard molar enthalpy of vaporization, at T = 298.15 K, $\Delta_l^g H_m^o$, of the methyl 1-methyl-2-pyrrolecarboxylate (M1M2PC). These experiments allowed the determination of its standard (p^o = 0.1 MPa) molar enthalpy of formation, in the gaseous phase, $\Delta_f H_m^o$ (g) = −(270.3 ± 2.2) kJ · mol^{-1}, at T = 298.15 K.

Additionally, the standard molar enthalpy of formation of M1M2PC was 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 one, giving us support to estimate the gas-phase enthalpies of formation of the methyl 1-methyl-3-pyrrolecarboxylate (M1M3PC), ethyl 1-methyl-2-pyrrolecarboxylate (E1M2PC) and ethyl 1-methyl-3-pyrrolecarboxylate (E1M3PC), that were not studied experimentally. The molecular structures of the four molecules were established and the structural parameters were determined at the B3LYP/6-31G(d) level of theory. Furthermore, all the results were interpreted in terms of enthalpic increments.

1. Introduction

Experimental and computational thermodynamic studies of pyrrole derivatives, with different substituent groups [1–13], have been developed in our Research Group during the last few years, with the main goal to correlate the effects of the corresponding molecular structures on the energetic characteristics of the compounds. Pyrrole moiety is the structural core of the naturally-occurring porphyrins, the tetrapyrrolic "pigments of life", which include the hemoglobin, porphyrins, corrins, vitamin B$_{12}$, the bile pigments and chlorophyll, playing an important role in respiration and photosynthesis processes [14–18]. Moreover, pyrrole and derivatives scaffolds are widely used as precursors in the synthesis of drugs with high therapeutical potential [19–30], polymers and new materials [31–37]. In this context, the knowledge of the molecular energetics of the core units is of great importance to understand the activity and the chemical behaviour of larger molecules involving them.

Following the same line of research, in the present work, we report an experimental and computational study on the energetic and structural properties of several alkyl 1-methylpyrrolecarboxylates (alkyl = methyl or ethyl), which are intended to be used as a building blocks of porphyrins, polypyrroles and medicines. An extensive characterization of molecules, in particular their energetic properties, is of high relevance, to a better knowledge about their reactivity and it is essential for studies of chemical equilibrium, kinetics and stability.

In this context, we report both the experimental standard (p° = 0.1 MPa) molar enthalpy of formation, in the liquid phase, and the standard molar enthalpy of vaporization, at T = 298.15 K, of the methyl 1-methyl-2-pyrrolecarboxylate (M1M2PC – figure 1) obtained, respectively, by static bomb combustion calorimetry and high temperature Calvet microcalorimetry. From these results, the standard (p° = 0.1 MPa) molar enthalpy of formation of the compound, in the gaseous phase, was derived. The G3(MP2)//B3LYP approach allowed the estimation of the gas-phase standard molar enthalpy of formation of M1M2PC, which was compared with the experimental value. These calculations were further extended to other alkyl 1-methylpyrrolecarboxylates, namely M1M3PC, E1M2PC and E1M3PC, whose study was not performed experimentally. Computationally, the molecular structures of the four molecules were established and the geometrical parameters were determined at the B3LYP/6-31G(d) level of theory.

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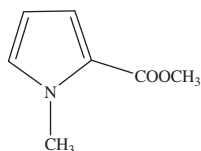
FIGURE 1. Structural formula for the methyl 1-methyl-2-pyrrolecarboxylate (M1M2PC).

2. Experimental

2.1. Compounds and purity control

The origin and purification details of the sample of M1M2PC used in this work are summarized in table 1. Its final purity was also checked by the percentage of carbon dioxide recovered during the combustion experiments; the average ratio of the mass of carbon dioxide recovered to those calculated from the mass of samples used in each experiment, together with the uncertainty (twice the standard deviation of the mean) was (1.0009 ± 0.0001).

The specific density of M1M2PC, used to calculate the true mass from apparent mass in air, was $\rho = 1.07 \text{ g} \cdot \text{cm}^{-3}$ [38]. The atomic weights used in this paper were those recommended by the IUPAC Commission in 2009 [39].

2.2. Combustion calorimetry

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, was used to measure the enthalpy of combustion of M1M2PC. Both the apparatus and the operating technique have been previously described [11,40,41].

The calorimetric system was calibrated following the procedure of Coops et al. [42] with benzoic acid NIST Standard Reference Material, sample 39j, [43]. 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 the standard deviation of the mean.

The liquid M1M2PC was burnt contained in previously weighed polyester bags made of melinex, 0.025 mm of thickness, $\Delta_c u^o$ (melinex) = $-(22902 \pm 5) \text{ J} \cdot \text{g}^{-1}$ [44]. The energetic effect for the amount of nitric acid produced in the combustion has been determined as it is reported in previous studies [11]. 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. The corrections to the standard state, ΔU_Σ, and the calculation of the standard massic energies of combustion of both compounds, $\Delta_c u^o$, were made following the procedure given by Hubbard et al. [45].

2.3. High temperature Calvet microcalorimetry

A high temperature Calvet microcalorimeter (Setaram HT 1000) was used, in this work, to measure the standard molar enthalpy of vaporization of the M1M2PC, through the drop-microcalorimetric technique for vacuum sublimation, described by Skinner et al. [46], for the sublimation of solid compounds and adapted, in our Laboratory, for liquid vaporizations [47]. The measuring procedure and a detailed description of the technique have been previously reported [48].

The microcalorimeter was calibrated making use of the standard molar enthalpy of vaporization of n-undecane (Aldrich, mass fraction purity > 0.99), $\Delta_l^g H_m^o$ (298.15 K) = (56.580 ± 0.566) kJ· mol^{-1} [49]. The calibration constant, k, of the calorimeter was obtained as the average of six independent experiments for the pre-defined temperature, $k(T = 360 \text{ K}) = (1.0437 \pm 0.0012)$; the uncertainty presented is the standard deviation of the mean.

3. Computational thermochemistry

Standard ab initio molecular orbital calculations, [50], were performed with the Gaussian 03 computer code [51], and the composite G3(MP2)//B3LYP approach was the methodology employed to compute the gas-phase enthalpies of all species considered [52].

The absolute enthalpies, at $T = 298.15$ K, were then used to estimate the enthalpy of formation of the compound studied experimentally (M1M2PC), by combining the enthalpy of the gas-phase working reactions (1) and (2) and the experimental enthalpies of formation of the molecules there included. The calculations were also extended to the M1M3PC (reactions (1) and (2)), E1M2PC (reactions (3) and (4)) and E1M3PC (reactions (3) and (4)), molecules that were not studied experimentally. The enthalpies of formation of the four referred compounds have also been estimated from the respective computed enthalpy of atomization reaction, at $T = 298.15$ K:

$$(1)$$

$$(2)$$

$$(3)$$

$$(4)$$
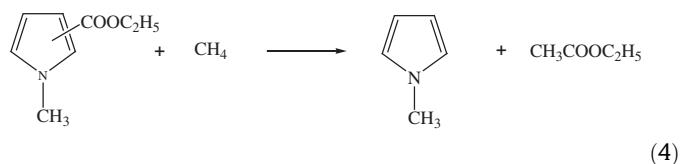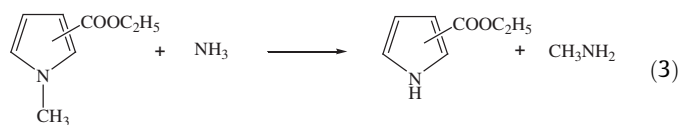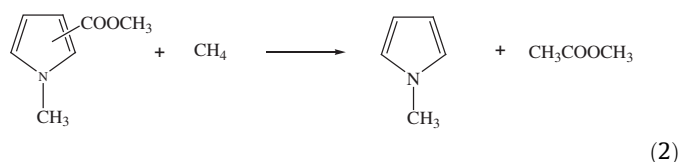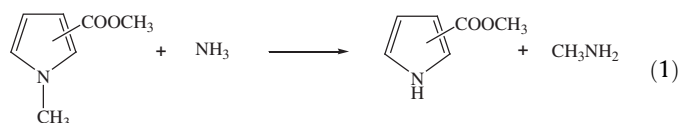
TABLE 1
Provenance and purity details of the compound studied.

Chemical name	CAS	Provenance	Initial molar fraction purity	Purification method	Final molar fraction purity	Analysis method
Methyl 1-methyl-2-pyrrolecarboxylate (l)	37619-24-2	Alfa-Aesar	0.99	Distillation	0.9997	GC[a]

[a] Gas–liquid chromatography.

4. Experimental results

Table 2 lists the detailed results of the combustion experiments of the M1M2PC. The values of the energy associated with the iso-thermal bomb process, $\Delta U(\text{IBP})$, were calculated by means of the equation (5), in which $c_p(H_2O, l)$ is the massic heat capacity, at constant pressure, for the liquid water, Δm (H_2O) 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:

$$\Delta U(\text{IBP}) = -\{\varepsilon(\text{calor}) + c_p(H_2O,l) \cdot \Delta m(H_2O) + \varepsilon_f\}\Delta T_{ad} + \Delta U(\text{ign}). \quad (5)$$

The values of $\Delta_c u^o$ presented in table 2 refer to the idealized combustion reaction represented by equation (6):
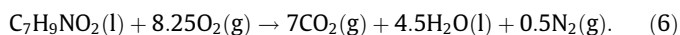
$$C_7H_9NO_2(l) + 8.25O_2(g) \rightarrow 7CO_2(g) + 4.5H_2O(l) + 0.5N_2(g). \quad (6)$$

Table 3 presents the derived values of the standard molar energy and enthalpy of combustion, $\Delta_c U_m^o(l)$ and $\Delta_c H_m^o$ (l) respectively, along with the standard molar enthalpy of formation, $\Delta_f H_m^o$ (l), for the M1M2PC, in the liquid phase, at $T = 298.15$ K, which was derived from the value of $\Delta_c H_m^o$ (ll) and from the following standard molar enthalpies formation, at $T = 298.15$ K: $\Delta_f H_m^o$ (H_2O, l) $= -(285.830 \pm 0.042)$ kJ·mol^{-1} and $\Delta_f H_m^o$ (CO_2, g) $= -(393.51 \pm 0.13)$ kJ·mol^{-1} [53].

According to Rossini [54] and Olofsson [55], 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 vaporization, for the compound studied, are presented in table 4. The corrective term $\Delta_{298.15\,K}^T H_m^o(g)$, used to correct the enthalpy of vaporization, at the experimental temperature T, to $T = 298.15$ K, was calculated through the equation (7):

$$\Delta_{298.15\,K}^T H_m^o(g) = \int_{298.15\,K}^T C_{p,m}^o(g)\,dT. \quad (7)$$

The gas-phase molar heat capacities of M1M2PC (equation (8)) 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) [56]. The values of $C_{p,m}^o(g) = f(T)$ obtained, between temperatures 150 K and 600 K, are listed in the Supporting information, table S1.

$$C_{p,m}^o(g)/\ (J \cdot K^{-1} \cdot mol^{-1}) = -6.37293 \times 10^{-7}(T/K)^3$$
$$+ 5.66480 \times 10^{-4}(T/K)^2 + 2.54000 \times 10^{-1}(T/K)$$
$$+ 50.617 \quad (R^2 = 0.99996). \quad (8)$$

The uncertainty associated with the value of $\Delta_l^g H_m^o(T = 298.15\,K)$ is twice the overall standard deviation of the mean and include the uncertainties in calibration and in the gas-phase molar heat capacity.

TABLE 2
Standard ($p^o = 0.1$ MPa) massic energy of combustion of methyl 1-methyl-2-pyrrolecarboxylate, at $T = 298.15$ K.

	1	2	3	4	5	6
m (CO_2, total)/g	1.35011	1.37842	1.44725	1.54754	1.53874	1.49877
m(cpd)/g	0.56509	0.57808	0.60961	0.65460	0.64801	0.62979
m'(fuse)/g	0.00306	0.00292	0.00286	0.00316	0.00355	0.00353
m''(melinex)/g	0.04110	0.04100	0.04062	0.04071	0.04296	0.04313
ΔT_{ad}/K	1.00536	1.02698	1.07899	1.15429	1.14683	1.11670
ε_f/J·K^{-1}	15.64	15.69	15.75	15.84	15.83	15.78
$\Delta m(H_2O)$/g	0	0	0	0	0	0
$-\Delta U(\text{IBP})^a$/J	16095.82	16441.88	17274.83	18480.43	18361.02	17878.54
$\Delta U(\text{fuse})$/J	49.69	47.42	46.45	51.32	57.65	57.33
$\Delta U(\text{melinex})$/J	941.20	938.92	930.24	932.29	983.92	987.81
$\Delta U(HNO_3)$/J	31.48	29.80	32.55	36.59	36.48	36.42
$\Delta U(\text{ign})$/J	0.94	1.09	0.93	1.07	1.02	1.03
ΔU_Σ/J	10.52	10.77	11.34	12.18	12.11	11.76
$-\Delta_c u^o$/J·g^{-1}	26655.81	26665.81	26663.36	26654.52	26652.15	26652.09

$m(CO_2$, 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; $\Delta U(\text{IBP})$ 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 the melinex; $\Delta U(HNO_3)$ 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
Derived standard ($p^o = 0.1$ MPa) molar values for the liquid compound, at $T = 298.15$ K.

Compound	$-\Delta_c U_m^o(l)$/kJ·mol^{-1}	$-\Delta_c H_m^o(l)$/kJ·mol^{-1}	$-\Delta_f H_m^o(l)$/kJ·mol^{-1}
Methyl 1-methyl-2-pyrrolecarboxylate	3709.4 ± 1.6	3711.3 ± 1.6	329.5 ± 1.9

TABLE 4
Standard ($p^o = 0.1$ MPa) molar enthalpy of vaporization, $\Delta_l^g H_m^o$, for the compound studied, at $T = 298.15$ K, determined by Calvet microcalorimetry.

Compound	Number of experiments	T/K	$\Delta_l^{g,T} H_m^o$/kJ·mol^{-1}	$\Delta_{29815K}^T H_m^o$/kJ·mol^{-1}	$\Delta_l^g H_m^o(T = 298.15K)$/kJ·mol^{-1}
Methyl 1-methyl-2-pyrrolecarboxylate	5	360.0	69.9 ± 0.2	10.6887 ± 0.0006	59.2 ± 1.2

5. Discussion

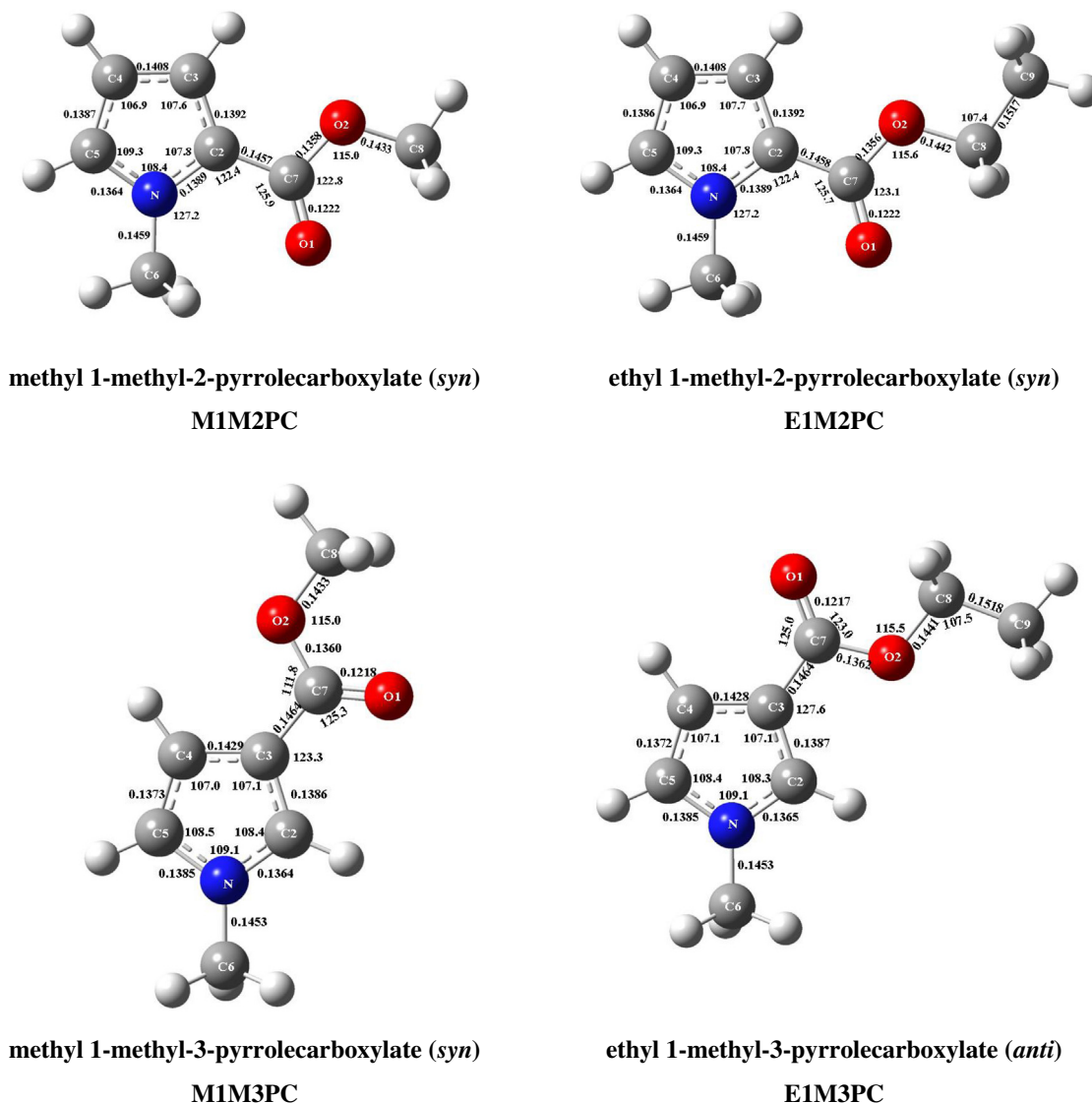### 5.1. Gas-phase – molecular structures

The most stable conformations of M1M2PC, M1M3PC, E1M2PC and E1M3PC, optimized at the B3LYP/6-31G(d) level of theory, from the G3(MP2)//B3LYP calculations are shown in figure 2. Selected structural details are given in those figures.

At the G3(MP2)//B3LYP level, the N−H,O-*syn* is the preferred conformation for M1M2PC, M1M3PC and E1M2PC, in agreement with the corresponding non-methylated analogues in the *N*- position, the methyl 2-pyrrolecarboxylate (M2PC), methyl 3-pyrrole-carboxylate (M3PC) and ethyl 2-pyrrolecarboxylate (E2PC) [12], as well as with other substituted pyrroles [2,3,10]. The N−H,O-*anti* conformation is 8.4, 0.3 and 8.0 kJ · mol⁻¹ less stable than the N−H,O-*syn*, for M1M2PC, M1M3PC and E1M2PC, respectively. For E1M3PC, the N−H,O-*anti* conformation is slightly more stable than the *syn* structure, by 0.7 kJ · mol⁻¹; the same conformation has already been found for the E3PC [12].

The enthalpic differences between both conformations for M3PC and ethyl 3-pyrrolecarboxylate (E3PC) and the corresponding analogues M1M3PC and E1M3PC are similar and very small (≈0.5 kJ · mol⁻¹); for the 2- pyrrole substituted M2PC and E2PC, as well as for the M1M2PC and E1M2PC, the differences are higher, about 4 kJ · mol⁻¹ and 8 kJ · mol⁻¹, respectively, which is also in agreement with the results previously reported [2,3,10].

In the optimized structures of M1M2PC, M1M3PC and E1M3PC obtained in this work, the alkoxycarbonyl group is *syn* with respect to the pyrrole N atom of the heterocyclic ring, whereas for E1M2PC the ethoxycarbonyl group is *anti*, similarly with the analogues M2PC, M3PC, E2PC and E3PC [12].

The electron-withdrawing character of the alkoxycarbonyl group affects the π-conjugation in the pyrrole ring, causing some asymmetries and changes in the strength of the adjacent bonds to the atoms in which this group is attached, and, consequently, an alteration of the bond lengths. In M1M2PC and E1M2PC, the N-C2 bond lengths (0.1389 nm, for both) are higher than for the corresponding 3-isomers, M1M3PC and E1M3 PC (0.1364 and

methyl 1-methyl-2-pyrrolecarboxylate (*syn*)

M1M2PC

ethyl 1-methyl-2-pyrrolecarboxylate (*syn*)

E1M2PC

methyl 1-methyl-3-pyrrolecarboxylate (*syn*)

M1M3PC

ethyl 1-methyl-3-pyrrolecarboxylate (*anti*)

E1M3PC

FIGURE 2. B3LYP/6-31G(d) optimized most stable configurations for the methyl 1-methyl-2-pyrrolecarboxylate (*syn*), ethyl 1-methyl-2-pyrrolecarboxylate (*syn*), methyl 1-methyl-3-pyrrolecarboxylate (*syn*) and ethyl 1-methyl-3-pyrrolecarboxylate (*anti*). Selected bond lengths (nm) and bond angles (deg) are included.

0.1365 nm, respectively), i.e., these bonds are weaker than in the 3-isomers due to the proximity of the alkoxycarbonyl group, that removes electronic density from the ring. A similar behaviour is observed for the 3-isomers, in which the C3–C4 bond lengths are higher than for the 2-isomers.

For the four calculated structures, presented in figure 2, the alkoxycarbonyl group is coplanar with the pyrrole ring. The dihedral angle between the pyrrole ring and the alkoxycarbonyl plane ranges from 0.004° to 0.2°. These molecules, optimized at the B3LYP/6-31G(d) level of theory, adopt a nearly planar structure, with the exception of the H atoms of the alkyl group and those of the N–CH₃ group; the sum of the endocyclic angles of the pyrrole ring is 540°.

No structural data for these alkyl 1-methylpyrrolecarboxylates have been found in the literature for comparison with our results.

TABLE 5
Experimental and G3(MP2)//B3LYP computed gas-phase enthalpies of formation, of the alkyl 1-methyl-pyrrolecarboxylates studied, at T = 298.15 K.[a]

$-\Delta_f H_m^o(g)/kJ \cdot mol^{-1}$					
Reaction	M1M2PC	M1M3PC	Reaction	E1M2PC	E1M3PC
1	270.4 (0.1)	268.3	3	304.5	301.1
2	272.4 (2.1)	269.5	4	303.2	299.8
Atom.	268.7 (−1.6)	265.7	Atom.	302.0	298.6
Exp.	270.3 ± 2.2				

[a] Enthalpic differences between the experimental and computed values are given in parentheses.
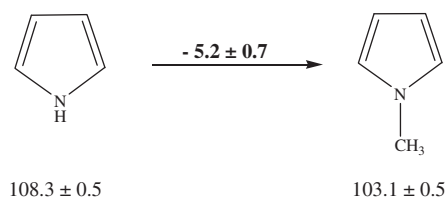
FIGURE 3. Enthalpic increments (kJ · mol⁻¹) of the introduction of a –CH₃ group in the *N*–position of pyrrole to yield 1-methylpyrrole [57].
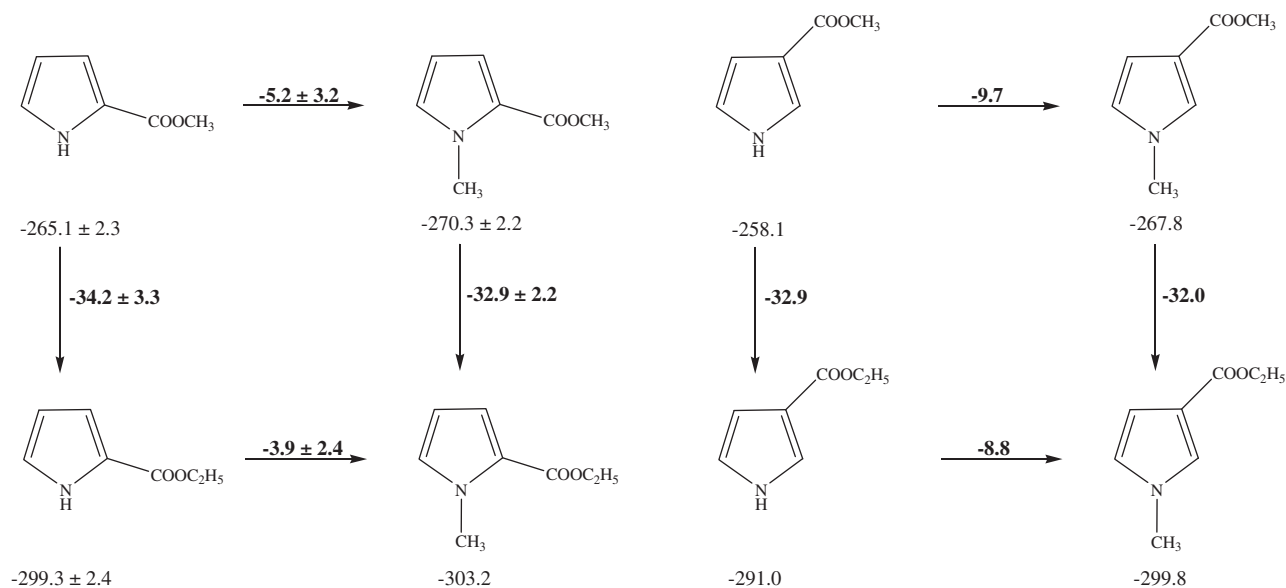
5.2. Gas-phase experimental and computational enthalpies of formation

The experimental gas-phase standard ($p°$ = 0.1 MPa) molar enthalpy of formation, at T = 298.15 K, of the M1M2PC, derived from the respective standard molar enthalpy of formation, in the liquid phase and the standard molar enthalpy of vaporization is presented in table 5. The computational gas-phase molar enthalpies of formation of M1M2PC, M1M3PC, E1M2PC and E1M3PC, estimated by combining the respective enthalpies of the working reactions, at T = 298.15 K, computed at the G3(MP2)//B3LYP level, with the experimental enthalpies of formation of the auxiliary molecules and atoms there included, are also registered in table 5. All the experimental $\Delta_f H_m^o$ (g) for the auxiliary species involved in the working reactions as well as their computed G3(MP2)//B3LYP enthalpies are presented in table S2, in the Supporting information.

Regarding the values of the calculated gas-phase enthalpies of formation of M1M2PC, one can easily see that there is an excellent agreement between the experimental and estimated data, with maximum enthalpic difference of 2.1 kJ · mol⁻¹ (reaction 2). The best estimate is achieved when the reaction described by equation 1 is considered, with a deviation only of 0.1 kJ · mol⁻¹. It should be pointed out here that the deviations obtained considering the three working reactions fall within the experimental uncertainty and that these three different reactions lead to estimated results that are in close agreement with the experimental value, supporting it and clearly showing that the composite G3(MP2)//B3LYP method seem to work very well with this kind of compounds, as was already shown in previous studies of pyrrole derivatives.

Due to the excellent agreement found for M1M2PC, between the experimental and calculated data, we have decided to extend the calculations of $\Delta_f H_m^o$(g) to the isomers for which the study was not performed experimentally, namely M1M3PC, E1M2PC and E1M3PC, using the corresponding gas-phase enthalpies of reactions, as well as the atomization reactions. Through the estimated results, which are summarized in table 5, one can see, once more, that similar values are obtained applying different working reactions; a mean value for the $\Delta_f H_m^o$ (g) of M1M3PC, E1M2PC and E1M3PC as −267.8 kJ · mol⁻¹, −303.2 kJ · mol⁻¹ and −299.8 kJ · mol⁻¹, respectively, is suggested to be used in future works.

FIGURE 4. Enthalpic increments (kJ · mol⁻¹) of the introduction of a –CH₃ group in the *N*– position of the alkyl pyrrolecarboxylates (alkyl = methyl or ethyl) [12].

The calculated values by the G3(MP2)//B3LYP method can have a deviation as large as ± 5.2 kJ · mol^{-1} [52]. Despite the deviation of the values calculated by the G3(MP2)//B3LYP, the data obtained by using different working reactions (table 5) are within that interval and in agreement with the experimental result.

The results reported in this work, combined with other values published in the literature, enable us to determine the enthalpic increments for the insertion of a –CH$_3$ group in the in the *N*– position of pyrrole [57] and in alkyl pyrrolecarboxylates (alkyl = - methyl or ethyl) [12]. The schemes are presented, respectively, in figures 3 and 4.

The presence of a methyl group in the *N*– position of pyrrole ring, methyl 2-pyrrolecarboxylate and ethyl 2-pyrrolecarboxylate produces, within the experimental uncertainties, the same stabilizing enthalpic effect, as it is shown in figures 3 and 4. The "entrance" of this group slightly stabilizes the rings, by ≈5 kJ · mol^{-1}, and this may be related with the inductive electronic density donor character of the methyl group. The introduction of a –CH$_3$ group in the corresponding 3-isomers, methyl 3-pyrrolecarboxylate and ethyl 3-pyrrolecarboxylate yielding the methyl 1-methyl-3-pyrrolecarboxylate and ethyl 1-methyl-3-pyrrolecarboxylate, respectively, causes a higher stabilization than for the 2-isomers, ca. 9 kJ · mol^{-1}. It is also possible to see in the scheme of figure 4 that the enthalpic increment for the presence of a methylene group, –CH$_2$–, in the methoxycarbonyl substituent to yield the respective ethoxycarbonyl, for all the compounds considered, is almost the same, ≈ –33 kJ · mol^{-1}.

6. Conclusions

The gas-phase standard molar enthalpy of formation of M1M2PC was obtained by combining results from calorimetric and computational techniques. Both experimental and computed values compare very well. The computational study was extended to the isomers M1M3PC, E1M2PC and E1M3PC, and a mean $\Delta_f H_m^o$ (g) values were obtained. We believe that these computed values are accurate enough to be included in future compilations.

The computational analysis of the four molecules, obtained at the B3LYP/6-31G(d) level of theory, allowed a better insight about their molecular structure and geometrical parameters. For M1M2PC, M1M3PC and E1M2PC, the N−H,O-*syn* conformation is more stable than the *anti* structure. The most stable conformation adopted by E1M3PC is the N−H,O-*anti*, which is only 0.7 kJ · mol^{-1} more stable than the *syn* orientation. The analysis of the results, in terms of enthalpic increments, show that they correlate well between each other and with available literature values for structural related compounds.

Acknowledgments

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jct.2013.08.004.

References

[1] A.F.L.O.M. Santos, J.R.B. Gomes, M.A.V. Ribeiro da Silva, J. Phys. Chem. A 113 (2009) 3630–3638.
[2] A.F.L.O.M. Santos, M.A.V. Ribeiro da Silva, J. Phys. Chem. A 113 (2009) 9741–9750.
[3] M.A.V. Ribeiro da Silva, A.F.L.O.M. Santos, J. Phys Chem. B 114 (2010) 2846–2851.
[4] A.F.L.O.M. Santos, M.A.V. Ribeiro da Silva, J. Chem. Thermodyn. 42 (2010) 734–741.
[5] A.F.L.O.M. Santos, M.A.V. Ribeiro da Silva, J. Chem. Thermodyn. 42 (2010) 1016–1023.
[6] A.F.L.O.M. Santos, M.A.V. Ribeiro da Silva, J. Chem. Thermodyn. 42 (2010) 1079–1086.
[7] A.F.L.O.M. Santos, M.A.V. Ribeiro da Silva, J. Chem. Thermodyn. 42 (2010) 1441–1450.
[8] M.A.V. Ribeiro da Silva, A.F.L.O.M. Santos, J. Phys. Chem. B 114 (2010) 16214–16222.
[9] A.F.L.O.M. Santos, M.A.V. Ribeiro da Silva, J. Chem. Thermodyn. 43 (2011) 1480–1487.
[10] A.F.L.O.M. Santos, M.A.V. Ribeiro da Silva, J. Phys. Chem. B 115 (2011) 12549–12557.
[11] A.F.L.O.M. Santos, M.A.V. Ribeiro da Silva, J. Chem. Thermodyn. 48 (2012) 194–200.
[12] A.F.L.O.M. Santos, M.A.V. Ribeiro da Silva, J. Phys. Chem. A 117 (2013) 5195–5204.
[13] A.F.L.O.M. Santos, M.A.V. Ribeiro da Silva, Struct. Chem., (2013), accepted for publication, doi: 10.1007/s11224-013-0288-z.
[14] A.R. Battersby, E. McDonald, Biosynthesis of porphyrins, chlorins and corrins, in: K.M. Smith (Ed.), Porphyrins and Metalloporphyrins, Elsevier, Amsterdam, 1975 (Chapter 3).
[15] H. Falk, The Chemistry of Linear Oligopyrroles and Bile Pigments, Springer, Berlin, 1989.
[16] A.R. Battersby, Nat. Prod. Rep. 17 (2000) 507–526.
[17] F.J. Leeper, Nat. Prod. Rep. (1989) 171–203.
[18] A.I. Scott, Pure Appl. Chem. 53 (1981) 1215–1232.
[19] J. Lehuédé, B. Fauconneau, L. Barrier, M. Ourakow, A. Piriou, J.-M. Vierfond Eur, J. Med. Chem. 34 (1999) 991–996.
[20] R.W. Bürli, D. McMinn, J.A. Kaizerman, W. Hu, Y. Ge, Q. Pack, V. Jiang, M. Gross, M. Garcia, R. Tanaka, H.E. Moser Bioorg, Med. Chem. Lett. 14 (2004) 1253–1257.
[21] R.W. Bürli, P. Jones, D. McMinn, Q. Le, J.-X. Duan, J.A. Kaizerman, S. Difuntorum, H.E. Moser Bioorg, Med. Chem. Lett. 14 (2004) 1259–1263.
[22] R. Jonas, M. Klockow, I. Lues, H. Prücher, H.J. Schliep, H. Wurziger, H. Eur, J. Med. Chem. 28 (1993) 129–140.
[23] W. von der Saal, J.-P. Hölck, W. Kampe, A. Mertens, B. Müller-Beckmann, B. J. Med. Chem. 32 (1989) 1481–1491.
[24] W.A. Denny, G.W. Rewcastle, B.C. Baguley, J. Med. Chem. 33 (1990) 814–819.
[25] V.J. Demopoulos, E. Rekka, J. Pharm. Sci. 84 (1995) 79–82.
[26] M. Del Poeta, W.A. Schell, C.C. Dykstra, S. Jones, R.R. Tidwell, A. Czarny, M. Bajic, M. Bajic, A. Kumar, D. Boykin, J.R. Perfect Antimicrob, Agents Chemother. 42 (1998) 2495–2502.
[27] S. Kirner, P.E. Hammer, D.S. Hill, A. Altmann, I. Fischer, L.J. Weislo, M. Lanahan, K.-H. Pée, J.M. Lingon, J. Bacteriol. 180 (1998) 1939–1943.
[28] R. Bonnett, Chem. Soc. Rev. 24 (1995) 19–33.
[29] A.J.F.N. Sobral, A.M.d'A. Rocha-Gonsalves, J. Porphyrins, Phthalocyanines 5 (2001) 428–430.
[30] A.J.F.N. Sobral, A.M.d'A. Rocha-Gonsalves, J. Porphyrins, Phthalocyanines 5 (2001) 861–866.
[31] T.A. Skotheim (Ed.), Handbook of Conducting Polymers, vol. 1, Marcel Dekker, New York, 1986.
[32] V.C. Smith, S.V. Batty, T. Richardson, K.A. Foster, R.A.W. Johnstone, A.J.F.N. Sobral, A.M.d'A. Rocha-Gonsalves, Thin Solid Films 284–285 (1996) 911–914.
[33] T. Richardson, V.C. Smith, R.A.W. Johnstone, A.J.F.N. Sobral, A.M.d'A. Rocha-Gonsalves, Thin Solid Films 327–329 (1998) 315–320.
[34] S. Cosnier, A. Walter, F.-P. Monforts, J. Porphyrins Phthalocyanines 2 (1998) 39–43.
[35] C. Di Natale, R. Paolesse, A. Macagnano, A. Mantini, C. Goletti, A. D'Amico, Sens. Actuat. B 52 (1998) 162–168.
[36] D. Kumar, R.C. Sharma, Eur. Polym. J. 34 (1998) 1053–1060.
[37] J. Roncali, Chem. Rev. 97 (1997) 173–205.
[38] www.chemnet.com (April 29, 2013).
[39] M.E. Wieser, T.B. Coplen, Pure Appl. Chem. 83 (2011) 359–396.
[40] M.A.V. Ribeiro da Silva, M.D.M.C. Ribeiro da Silva, G. Pilcher, Rev. Port. Quim. 26 (1984) 163–172.
[41] M.A.V. Ribeiro da Silva, M.D.M.C. Ribeiro da Silva, G. Pilcher, J. Chem. Thermodyn. 16 (1984) 1149–1155.
[42] J. Coops, R.S. Jessup, K.G. van Nes, in: F.D. Rossini (Ed.), Experimental Thermochemistry, vol. 1, Interscience: New York, 1956 (Chapter 3).
[43] Certificate of Analysis Standard Reference Material 39j Benzoic Acid Calorimetric Standard. NBS, Washington (1995).
[44] H.A. Skinner, A. Snelson, Trans. Faraday Soc. 56 (1960) 1776–1783.
[45] W.N. Hubbard, D.W. Scott, G. Waddington in: F.D. Rossini (Ed.), Experimental Thermochemistry, vol. 1, Interscience, New York, 1956 (Chapter 5).
[46] F.A. Adedeji, D.L.S. Brown, J.A. Connor, M. Leung, M.I. Paz-Andrade, H.A. Skinner, J. Organomet. Chem. 97 (1975) 221–228.

[47] M.A.V. Ribeiro da Silva, M.A.R. Matos, L.M.P.F. Amaral, J. Chem. Thermodyn. 27 (1995) 565–574.
[48] L.M.N.B.F. Santos, B. Schröder, O.O.P. Fernandes, M.A.V. Ribeiro da Silva, Thermochim. Acta 415 (2004) 15–20.
[49] R. Sabbah, A. Xu-wu, J.S. Chickos, M.L.P. Leitão, M.V. Roux, L.A. Torres, Thermochim. Acta 331 (1999) 93–204.
[50] W.J. Hehre, L. Radom, P.v.R. Schleyer, J.A. Pople, *Ab Initio* Molecular Orbital Theory, Wiley, New York, 1986.
[51] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J.

Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision C.01, Gaussian, Inc., Wallingford CT, 2004.
[52] A.G. Baboul, L.A. Curtiss, P.C. Redfern, K. Raghavachari, J. Chem. Phys. 110 (1999) 7650–7657.
[53] J.D. Cox, D.D. Wagman, V.A. Medvedev, CODATA Key Values for Thermodynamics, Hemisphere, New York, 1989.
[54] F.D. Rossini, in: F.D. Rossini (Ed.), Experimental Thermochemistry, vol. 1, Interscience: New York, 1956 (Chapter 14).
[55] G. Olofsson, in: S. Sunner, M. Månsson (Eds.), Combustion Calorimetry, Pergamon Press, Oxford, 1979 (Chapter 6).
[56] K.K. Irikura, THERMO.PL, National Institute of Standards and Technology, 2002.
[57] J.B. Pedley, Thermochemical Data and Structures of Organic Compounds, vol. 1, TRC Data Series, College Station, TX, 1994.

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