Journal of Thermal Analysis and Calorimetry, Vol. 90 (2007) 3, 865–871

THERMOCHEMICAL PROPERTIES OF THREE PIPERIDINE DERIVATIVES
1-Benzyl-4-piperidinol, 4-benzylpiperidine and 4-piperidine-piperidine

M. A. V. Ribeiro da Silva[*] *and Joana I. T. A. Cabral*

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

The standard (p^o=0.1 MPa) molar energies of combustion for the crystalline 1-benzyl-4-piperidinol and 4-piperidine-piperidine, and for the liquid 4-benzylpiperidine, were measured by static bomb calorimetry, in oxygen, at T=298.15 K. The standard molar enthalpies of sublimation or vaporization, at T=298.15 K, of these three compounds were determined by Calvet microcalorimetry.

Those values were used to derive the standard molar enthalpies of formation, at T=298.15 K, in their condensed and gaseous phase, respectively.

Keywords: *4-benzylpiperidine, 1-benzyl-4-piperidinol, Calvet microcalorimetry, combustion calorimetry, enthalpy of combustion, enthalpy of formation, enthalpy of sublimation, enthalpy of vaporization, 4-piperidine-piperidine*

Introduction

The study of the molecular energetics of nitrogen heterocyclic compounds has been one of our main interests [1, 2] and so we have reported thermochemical properties of quinolines [3–13], pyridines [14–18], imidazols and pyrazols [19–25], phthalimides [26, 27] and pyrazines [28]. These kinds of compounds have a wide and important range of practical applications, from the heavy chemical industry to the synthesis of pharmacological drugs, either as reactants, solvents or being units of molecular chemical structure of the final compounds, not to mention their everyday more important environmental impact. More specifically, cyclic amines are a very important class of chemicals with a significant biological importance.

Recently we have started the thermochemical study of several piperidine derivatives [29–35], as the piperidine ring being a structural element of many natural products and drugs, it is possible to find innumerable publications of studies about its properties and applications in industry, biology and medicine. As part of this work, the present paper reports the experimental determination of the standard molar enthalpies of formation in condensed, and gaseous phases of 1-benzyl-4-piperidinol **(A)**, 4-benzylpiperidine **(B)** and 4-piperidine-piperidine **(C)** (Fig. 1). Their respective standard molar enthalpies of vaporization or sublimation are also reported.

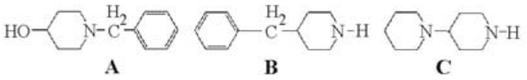


Fig. 1 Structural formula for 1-benzyl-4-piperidinol **(A)**, 4-benzylpiperidine **(B)** and 4-piperidine-piperidine **(C)**

The standard (p^o=0.1 MPa) molar enthalpies of formation in the condensed state, at T=298.15 K, were determined from the values of the respective standard massic energies of combustion, while the standard molar enthalpies of vaporization or sublimation, at T=298.15 K, were measured by Calvet microcalorimetry. From these two sets of results, the standard molar enthalpies of formation in the gaseous state, at the temperature 298.15 K, were derived.

Experimental

Materials

Compounds and purity control

All the compounds, 1-benzyl-4-piperidinol [CAS 4727-72-4], 4-benzylpiperidine [CAS 31252-42-3] and 4-piperidine-piperidine [CAS 4897-50-1], were obtained commercially from Aldrich Chemical Co. 4-Benzylpiperidine was purified by repeated vacuum distillation and it was stored and handled under nitrogen atmosphere. 1-Benzyl-4-piperidinol and

---

[*] Author for correspondence: risilva@fc.up.pt

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

4-piperidine-piperidine were purified by repeated vacuum sublimations. Since these compounds shown to be hygroscopic, they were also handled under dry nitrogen atmosphere. The purity was checked by g.l.c., d.s.c and carbon dioxide recovery from the combustion measurements. The average ratios of the mass of carbon dioxide recovered after combustion, to that calculated from the mass of sample, were (values in percentage): for 1-benzyl-4-piperidinol (99.979±0.026), for 4-benzylpiperidine (100.045±0.019), and for 4-piperidine-piperidine (99.997±0.011), where the uncertainties are the standard deviations of the means.

Methods

Combustion calorimetry

The description of the calorimeter, subsidiary apparatus and technique used to measure the combustion energies of compounds has been reported in literature [36, 37]. The experiments were performed with an isoperibol static bomb calorimeter, with the compounds burnt in a twin-valve combustion bomb, Parr Instrument Company, type 1105, made of stainless steel, with an internal volume of 340 cm^3.

The solid compounds were pressed into pellet form and, as they were hygroscopic, it was necessary to seal them into Melinex polyester bags, with 0.025 mm thickness, to prevent the absorption of moisture during the experiment. The liquid 4-benzylpiperidine, which is also hygroscopic, was also closed into Melinex bags. All substances were burnt at an initial pressure of 3.04 MPa, with 1.00 cm^3 of water added to the bomb. For 4-piperidine-piperidine it was also necessary to use *n*-hexadecane (Aldrich Gold Label, mass fraction >0.999), stored under nitrogen, as a combustion auxiliary. The calorimeter temperatures were measured to $\pm 1\cdot 10^{-4}$ K, at time intervals of 10 s, with a quartz crystal thermometer (Hewlett Packard HP 2804A), interfaced to a PC. The ignition was made at T=298.150±0.001 K, by the discharge of a 1400 μF capacitor through the platinum ignition wire. A cotton tread fuse with empirical formula of $CH_{1.686}O_{0.843}$ was used. At the end of the experiment, the CO_2 produced in the combustions was determined, letting the gases produced in the combustions being through CO_2 recovering tubes, filled with carbosorb AS self-indicating. The amount of HNO_3 formed was determined by titration of the aqueous solution resulting from washing the inside of the bomb. If only a small quantity of carbon was formed inside the crucible, its amount was determined and taken into account for the calculation of the massic energy of combustion.

The energy equivalent of the calorimeter, determined from 6 independent experiments of combustion of Thermochemical Standard benzoic acid, sample NBS 39j, with $\Delta_c u = -26434\pm 3$ J g^{-1} [38], under the same experimental conditions used for the compounds, was found to be ε_{cal}= 15905.72±0.96 J K^{-1}. The calibration procedure followed the same as previously described [39], and the calibration results corrected to give the energy equivalents, ε_{cal}, corresponding to the average mass of water added to the calorimeter: 3119.6 g. The uncertainties quoted are the standard deviations of the mean.

The water added to the calorimetric vase was weighed with a Mettler PC 8000 balance, sensitivity $\pm 1\cdot 10^{-1}$ g, the necessary weighings for the combustion experiments were made in a Mettler Toledo 240 balance, sensitivity $\pm 1\cdot 10^{-5}$ g, and the CO_2 recovery tubes were weighed with a Mettler Toledo AT201 balance, sensitivity $\pm 1\cdot 10^{-4}$ g.

Microcalorimetry Calvet

The standard molar enthalpy of vaporization of 4-benzylpiperidine and the standard molar enthalpies of sublimation of 1-benzyl-4-piperidinol and 4-piperidine-piperidine were determined with a Calvet High Temperature Microcalorimeter (Setaram, HT 1000D) using for liquid compound a similar technique [40] to that described for the sublimation of solids by Skinner *et al.* [41]. The apparatus and the detailed technique description can be found in literature [42].

In the experiments, samples of about 5 mg of compound, contained in a thin glass capillary tube sealed at one end, were dropped from room temperature into the hot zone of the calorimeter, held at a predefined convenient temperature for the study of the vaporization or sublimation of the compounds, T, and then removed from the hot zone by vacuum vaporization or sublimation, depending on the compound. The thermal corrections for the glass capillaries were made by dropping tubes of nearly equal mass into each of the twin cells.

In this work, the calorimeter was held at T=339 K for 4-benzylpiperidine and at T=358 K for 1-benzyl-4-piperidinol and 4-piperidine-piperidine. At T=339 K, the calibration of the calorimeter was made with *n*-undecane, 99+, supplied by Aldrich Chemical Co., using the value of $\Delta_{l}^{g}H_{m}^{o}$= 56.580±0.566 kJ mol^{-1} for the standard molar enthalpy of vaporization of the *n*-undecane at T=298.15 K [43]. From 6 independent experiments, the value of the calibration constant for this temperature was k_{cal} (T=339 K)=0.9794±0.0020, with the uncertainty as the standard deviation of the mean. At

T=358 K, the value of the calibration constant was found to be k_{cal} (T=358 K)=1.0065±0.0079, determined by sublimation of naphthalene, using the value of$\Delta^{\mathrm{g}}_{\mathrm{cr}}H^{\mathrm{o}}_{\mathrm{m}}$ (naphthalene, cr)=72.60±0.60 kJ mol^{-1} [43], at T=298.15 K. The values of the enthalpies of vaporization/sublimation of n-undecane and naphthalene, at the temperature T of the calibration experiments, were calculated from their values at T=298.15 K using literature values of $\Delta^{\mathrm{T}}_{298.15\ \mathrm{K}}H^{\mathrm{o}}_{\mathrm{m}}$(g), from Stull *et al.* [44]. The experimental procedure for the calibration experiments was the same as the one used for the experiments with the compounds.

Results and discussion

Results for a typical combustion experiment of each compound are given in Table 1, where $\Delta m(H_2O)$ is the deviation of the mass of water added to the calorimeter from 3119.6 g, with the internal energy for the isothermal bomb process, $\Delta U_{\mathrm{I.B.P.}}$, calculated according to the equation: $\Delta U_{\mathrm{I.B.P.}}= -\{\varepsilon_{\mathrm{cal}}+\Delta m_{\mathrm{H_2O}}\,c_{\mathrm{p}}(\mathrm{H_2O,\ l})+\varepsilon_{\mathrm{f}}\}\Delta T_{\mathrm{ad}}+\Delta U_{\mathrm{ignition}}$, and ΔU_{Σ} is the correction to the standard state calculated by the procedure of Hubbard *et al.* [45]. ΔU(melinex) is the energy of combustion of the Melinex used in each experiment, corrected for the mass fraction of water w=0.0032 [46] and using the value of the massic energy of combustion of Melinex as $\Delta_{\mathrm{c}}u^{\mathrm{o}}$= –22902±5 J g^{-1}, measured by Snelson *et al.* [46]. The correction for the cotton thread fuse combustion, ΔU(fuse), was based on the value of its massic energy of combustion, $-\Delta_{\mathrm{c}}u^{\mathrm{o}}$=16250 J g^{-1} [39], a value that has been confirmed in our Laboratory. The corrections for nitric acid formation, $\Delta U(\mathrm{HNO_3})$, were based on –59.7 kJ mol^{-1}, for the molar energy of formation of 0.1 mol dm^{-3} $\mathrm{HNO_3}$(aq), from N_2, O_2 and H_2O(l) [47]. ΔU(ign) is the electrical energy supplied for ignition, and ΔU(carbon) the energy correction for the carbon residue soot formation, ΔU(carbon), was based on $\Delta_{\mathrm{c}}u^{\mathrm{o}}$= –33 J g^{-1} [48]. The massic energy of combustion of n-hexadecane, measured in our Laboratory was found to be $\Delta_{\mathrm{c}}u^{\mathrm{o}}$= –47160.8±4.1 J g^{-1} being used to calculate the correction, ΔU(hexadecane), for the n-hexadecane combustion. $\Delta_{\mathrm{c}}u^{\mathrm{o}}$ is the massic energy of combustion of the compound.

For each compound, an estimated pressure coefficient of massic energy, $(\partial u/\partial_{\mathrm{p}})_{\mathrm{T}}$, at T=298.15 K, was assumed to be –0.2 J g^{-1} MPa^{-1}, a typical value for most organic compounds [49], $\Delta_{\mathrm{c}}u^{\mathrm{o}}$ was calculated

Table 1 Results of a typical combustion experiment, at T=298.15 K

Experiment	1-Benzyl-4-piperidinol	4-Benzylpiperidine	4-Piperidine-piperidine
$m(\mathrm{CO_2}$, total)/g	1.47318	2.35912	2.10737
m(cpd)/g	0.50457	0.74322	0.70831
m(melinex)/g	0.03328	0.05043	0.03162
m(fuse)/g	0.00236	0.00261	0.00266
m(hexadecane)/g	–	–	0.05751
ΔT_{ad}/K	1.19791	1.96715	1.97752
ε_{f}/J K^{-1}	15.86	17.06	17.58
$\Delta m(H_2O)$/g	+0.1	0	+0.1
$-\Delta U(\mathrm{IBP})^{\mathrm{a}}$/J	19072.05	31321.60	31488.27
ΔU(melinex)/J	762.10	1155.03	724.18
ΔU(fuse)/J	38.33	42.39	43.20
ΔU(hexadecane)/J	–	–	2712.28
$\Delta U(\mathrm{HNO_3})$/J	23.70	42.03	58.33
ΔU(ign)/J	1.05	0.86	1.16
$-\Delta U$(carbon)/J	0	0	5.28
ΔU_{Σ}/J	9.30	14.99	12.46
$-\Delta_{\mathrm{c}}u^{\mathrm{o}}$/J g^{-1}	36146.86	40455.26	39450.38

$m(\mathrm{CO_2}$, total) is the total mass of carbon dioxide recovered in the combustion; m(cpd) is the mass of compound burnt in each experiment; m(melinex) is the mass of melinex used to enclose the compounds; m(fuse) is the mass of the cotton thread fuse; m(hexadecane) is the mass of hexadecane; ΔT_{ad} is the adiabatic temperature rise; ε_{f} is the energy equivalent of the calorimeter including the contents of the bomb in the final state; $\Delta m(H_2O)$ is the deviation of the mass of water added to the calorimeter from 3119.6 g; ΔU(IBP) is the energy change for isothermal combustion reaction under actual bomb conditions; ΔU(melinex) is the energy of combustion of the Melinex used in each experiment; ΔU(fuse) is the energy of combustion of the fuse (cotton); ΔU(hexadecane) is the energy of combustion of hexadecane; $\Delta(\mathrm{HNO_3})$ is the energy correction for the nitric acid formation; ΔU(ign) is the electrical energy supplied for ignition; ΔU(carbon) is the energy correction for the carbon residue soot formation; ΔU_{Σ} is the standard state correction; $\Delta_{\mathrm{c}}u^{\mathrm{o}}$ is the massic energy of combustion of the compound. $^{\mathrm{a}}\Delta U$(IBP) already includes ΔU(ign) by the procedure of Hubbard *et al.* [45], and the relative atomic masses used were those recommended by the IUPAC Commission in 2001 [50]. For all compounds studied, the individual values of $\Delta_c u^o$, together with the mean and its standard deviation, are given in Table 2.

Table 3 lists, for each compound, the derived standard molar values for the energy ($\Delta_c U^o_m$) and enthalpy ($\Delta_c H^o_m$) of combustion and the standard molar enthalpy of formation, $\Delta_f H^o_m$, in the condensed phase.

The uncertainties of standard molar energies and enthalpies of combustion are twice the final overall standard deviation of the mean, and include the uncertainties in calibration [51, 52] as well as the respective uncertainties of the auxiliary compounds used.

Table 2 Individual values of the massic energy of combustion, $\Delta_c u^o$, for the compounds, at T=298.15 K

1-Benzyl-4-piperidinol	4-Benzylpiperidine	4-Piperidine-piperidine
	$-\Delta_c u^o$/J g^{-1}	
36148.96	40455.26	39443.43
36146.86	40455.37	39450.38
36153.99	40462.51	39445.15
36152.68	40476.28	39458.20
36143.16	40449.41	39452.29
36139.90	40443.54	39444.07
	$-\langle\Delta_c u^o\rangle$/J g^{-1}	
36147.6±2.2	40457.1±4.6	39448.9±2.4

Table 3 Derived standard (p^o=0.1 MPa) molar energies of combustion, $\Delta_c U^o_m$, standard molar enthalpies of combustion, $\Delta_c H^o_m$, and standard molar enthalpies of formation for the compounds in the condensed phase, $\Delta_f H^o_m$(l or cr), at T=298.15 K

Compound	$-\Delta_c U^o_m$/ kJ mol^{-1}	$-\Delta_c H^o_m$/ kJ mol^{-1}	$-\Delta_f H^o_m$ (l or cr)/ kJ mol^{-1}
1-Benzyl-4-piperidinol (cr)	6913.9±2.1	6922.0±2.1	229.7±2.6
4-Benzyl-piperidine (l)	7090.9±2.5	7100.2±2.5	51.5±3.0
4-Piperidine-piperidine (cr)	6638.4±2.3	6648.3±2.3	145.1±2.7

The values of the standard molar enthalpies of formation in the condensed phase, $\Delta_f H^o_m$(l or cr), were derived from $\Delta_c H^o_m$, using the values, at T=298.15 K, of the standard molar enthalpies of formation of liquid water and gaseous carbon dioxide, respectively, as $\Delta_f H^o_m$(H_2O, l)= –285.830±0.042 kJ mol^{-1} [48] and $\Delta_f H^o_m$(CO_2, g)= –393.51±0.13 kJ mol^{-1} [48].

Results of the microcalorimetric determinations of the enthalpy of vaporization of 4-benzylpiperidine or the enthalpies of sublimation of 1-benzyl-4-piperidinol and 4-piperidine-piperidine, are given in Table 4. The enthalpies of vaporization or sublimation, at experimental temperature T, correspond to the mean values of 5 experiments with uncertainties given by their standard deviations. The observed molar enthalpies of vaporization or sublimation, $\Delta^{g,T}_{l\text{ or cr},298.15\text{ K}}H_m$, were corrected to T=298.15 K using $\Delta^{T}_{298.15\text{ K}}H^o_m$(g) estimated by a group scheme based on the values of Messerly *et al.* [53] and Stull *et al.* [44]. The schemes applied for these corrections are:

- 1-Benzyl-4-piperidinol=piperidine+cyclohexanol+methylamine+methylbenzene–cyclohexane–ammonia–methane;
- 4-Benzylpiperidine=piperidine+methylcyclohexane+methylbenzene–cyclohexane–methane;
- 4-Piperidine-piperidine=2×piperidine+methylamine–ammonia–methane,

which gives, at T=358.0 K, $\Delta^{358.0\text{ K}}_{298.15\text{ K}}H^0_m$(1-benzyl-4-piperidinol)=14.00 kJ mol^{-1}, at T=339.0 K, $\Delta^{339.0\text{ K}}_{298.15\text{ K}}H^0_m$(4-benzylpiperidine)=9.04 kJ mol^{-1} and at T=357.9 K, $\Delta^{357.9\text{ K}}_{298.15\text{ K}}H^0_m$(4-piperidine-piperidine)=12.61 kJ mol^{-1}.

The uncertainties associated to the standard enthalpies of vaporization or sublimation at T=298.15 K are twice the standard deviation of the mean and include the uncertainty associated with the calibration procedure.

Table 4 Microcalorimetric standard (p^o=0.1 MPa) molar enthalpies of vaporization or sublimation, at T=298.15 K

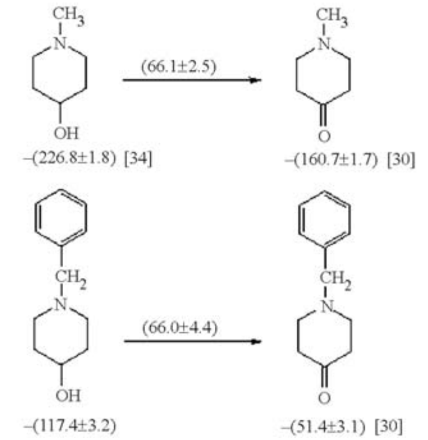
Compound	No. of experiments	T/K	$\Delta^{g,T}_{l\text{ or cr},298\text{ K}}H_m$/kJ mol^{-1}	$\Delta^{T}_{298.15\text{ K}}H^o_m$ (g)/kJ mol^{-1}	$\Delta^{g}_{l\text{ or cr}}H^o_m$/kJ mol^{-1}
1-Benzyl-4-piperidinol (cr)	5	358.0	126.33±0.18	14.00	112.3±1.8
4-Benzylpiperidine (l)	5	339.0	83.24±0.54	9.04	74.2±1.0
4-Piperidine-piperidine (cr)	5	357.9	101.21±0.72	12.61	88.6±1.9

Table 5 Derived standard (p^{o}=0.1 MPa) molar enthalpies of formation, $\Delta_f H^{o}_{m}$, and of vaporization or sublimation, $\Delta^{g}_{l or cr} H^{o}_{m}$, at T=298.15 K

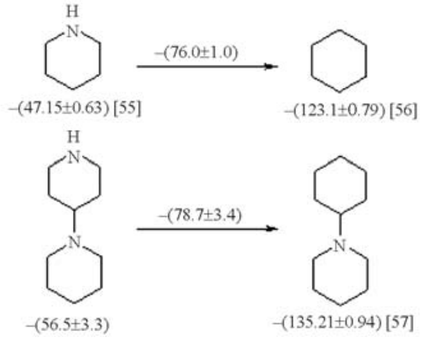
Compound	$\Delta_f H^{o}_{m}$ (l or cr)/kJ mol^{-1}	$\Delta^{g}_{l or cr} H^{o}_{m}$/kJ mol^{-1}	$\Delta_f H^{o}_{m}$ (g)/kJ mol^{-1}
1-Benzyl-4-piperidinol (cr)	–229.7±2.6	112.3±1.8	–117.4±3.2
4-Benzylpiperidine (l)	–51.5±3.0	74.2±1.0	22.7±3.2
4-Piperidine-piperidine (cr)	–145.1±2.7	88.6±1.9	–56.5±3.3

Table 6 Enthalpic difference between some benzyl and phenyl derivatives, δ(Bz-Ph) of nitrogen heterocycles

	$\Delta_f H^{o}_{m}$ (g)/ kJ mol^{-1}	Ref.	δ(Bz-Ph)/ kJ mol^{-1}
1-Phenyl-piperidine	70.3±1.4	[54]	–(20.0±4.1)
1-Benzyl-piperidine	[50.3±3.8]	Estimated in this work	
1-Phenyl-imidazole	264.7±4.3	[20]	–(20.6±5.5)
1-Benzyl-imidazole	244.1±3.4	[20]	
1-Phenyl-pirazole	291.4±4.5	[20]	–(15.1±5.4)
1-Benzyl-pirazole	276.3±2.9	[20]	
2-Phenyl-benzimidazole	258.0±2.5	[25]	–(18.8±5.1)
2-Benzyl-benzimidazole	239.2±4.4	[25]	



Scheme 1



Scheme 2

Conclusions

The derived standard molar enthalpies of formation, both in condensed and gaseous phase, and the standard molar enthalpy of vaporization or sublimation, are summarized in Table 5.

Considering the standard molar enthalpy of formation of 1-benzyl-4-piperidinol, and comparing it with the standard molar enthalpies of formation previously reported for 1-methyl-4-piperidone [30], 1-benzyl-4-piperidone [30] and 1-methyl-4-piperidinol [34], the enthalpic increment due to the oxidation of the hydroxyl to carbonyl group can be established as in Scheme 1.

Moreover, from the standard molar enthalpy of formation of 1-benzyl-4-piperidinol, and the enthalpic increment, δ(–OH), verified for the introduction of –OH group into position 4 of the piperidine ring [δ(–OH)= –167.7±2.0 kJ mol^{-1}] [34], the standard molar enthalpy of formation of 1-benzylpiperidine can be derived as $\Delta_f H^{o}_{m}$(g, 1-benzylpiperidine)=50.3±3.8 kJ mol^{-1}. This value can be used to compare the energetic increments for the substitution of a phenyl by benzyl substituents in the nitrogen heterocycles as it can be seen in Table 6, which shows that, within the experimental uncertainties, is the same in all cases.

Considering now the value of the standard molar enthalpy of formation obtained experimentally for 4-piperidine-piperidine and the literature values for piperidine, 1-cyclohexylpiperidine and cyclohexane, the enthalpic difference between the cyclohexane and piperidine is the same as the one verified for 4-piperidine-piperidine and 1-cyclohexenylpiperidine, as shown in the Scheme 2.

As a conclusion, the above presented relationships show an internal consistency of the experimental values presented in this paper, which gives a great confidence in these experimental values.

Acknowledgements

Thanks are due to Fundação para a Ciência e Tecnologia (FCT), Lisbon, Portugal and to FEDER for financial support to Centro de Investigação em Química, University of Porto. Joana I. T. A. Cabral thanks FCT and the European Social Fund (ESF) under the 3rd Community Support Framework (CSF) for the award of a PhD research grant (BD/5364/2001).

References

1 M. A. V. Ribeiro da Silva and M. A. R. Matos, Pure Appl. Chem., 69 (1997) 2295.
2 M. A. V. Ribeiro da Silva, Pure Appl. Chem., 71 (1999) 1257.
3 M. A. V. Ribeiro da Silva, M. J. S. Monte and M A. R. Matos, J. Chem. Thermodyn., 21 (1989) 159.
4 M. A. V. Ribeiro da Silva, M. A. R. Matos and M. J. S. Monte, J. Chem. Thermodyn., 22 (1990) 609.
5 M. A. V. Ribeiro da Silva and M. J. S. Monte, J. Chem. Thermodyn., 24 (1992) 715.
6 M. A. V. Ribeiro da Silva, M. A. R. Matos, M. J. S. Monte, M. C. B. Alves and J. M. A. P. Vieira, J. Chem. Thermodyn., 25 (1993) 579.
7 M. A. V. Ribeiro da Silva, M. A. R. Matos and L. M. P. F. Amaral, J. Chem. Thermodyn., 27 (1995) 565.
8 M. A. V. Ribeiro da Silva, M. L. C. C. H. Ferrão and A. M. R. O. Alves da Silva, J. Chem. Thermodyn., 27 (1995) 633.
9 M. A. V. Ribeiro da Silva, M. A. R. Matos and L. M. P. F. Amaral, J. Chem. Thermodyn., 27 (1995) 1141.
10 M. A. V. Ribeiro da Silva, M. A. R. Matos and L. M. P. F. Amaral, J. Chem. Thermodyn., 27 (1995) 1187.
11 M. A. V. Ribeiro da Silva, M. A. R. Matos and L. M. P. F. Amaral, J. Chem. Thermodyn., 29 (1997) 295.
12 M. A.V. Ribeiro da Silva, M. A. R. Matos and L. M. P. F. Amaral, J. Chem. Thermodyn., 37 (2005) 1312.
13 M. A.V. Ribeiro da Silva, M. A. R. Matos and L. M. P. F. Amaral, J. Chem Thermodyn., 38 (2006) 49.
14 M. A. V. Ribeiro da Silva, M. A. R. Matos and L. M. P. F. Amaral, J. Chem. Thermodyn., 29 (1997) 1535.
15 M. A. V. Ribeiro da Silva, M. A. R. Matos and L. M. P. F. Amaral, J. Chem. Thermodyn., 29 (1997) 1545.
16 M. A. V. Ribeiro da Silva, M. Agostinha R. Matos and G. Pilcher, J. Chem. Thermodyn., 24 (1992) 107.
17 M. A. V. Ribeiro da Silva, M. Agostinha R. Matos and C. M. A. Rio, J. Chem. Thermodyn., 29 (1997) 901.
18 J. R. B. Gomes, M. L. P. F. Amaral and M. A. V. Ribeiro da Silva, Chem. Phys. Lett., 406 (2005) 154.
19 M. A. V. Ribeiro da Silva, M. D. M. C. Ribeiro da Silva, M. A. R. Matos, P. Jiménez, M. V. Roux, J. Elguero, R. Claramunt, P. Cabildo and A. Sanchez-Migallón, J. Chem. Thermodyn., 31 (1999) 129.
20 O. Mó, M. Yáñez, M. V. Roux, P. Jiménez, J. Z. Dávalos, M. A.V. Ribeiro da Silva, M. D. M. C. Ribeiro da Silva, M. A. R. Matos, L. M. P. F. Amaral, A. Sánchez-Migallón, P. Cabildo, R. Claramunt, J. Elguero and J. F. Liebman, J. Phys. Chem., A 103 (1999) 9336.
21 M. A. V. Ribeiro da Silva, M. D. M. C. Ribeiro da Silva, M. A. R. Matos, P. Jiménez, M. V. Roux, M. A. Martin-Luengo, J. Elguero, R. Claramunt and P. Cabildo, J. Chem. Thermodyn., 32 (2000) 237.
22 O. Mó, M. Yáñez, J. Elguero, M. V. Roux, P. Jiménez, J. Z. Dávalos, M. A.V. Ribeiro da Silva, M. D. M. C. Ribeiro da Silva, P. Cabildo and R. Claramunt, J. Phys. Chem., A 107 (2003) 366.
23 M. A. V. Ribeiro da Silva, M. D. M. C. Ribeiro da Silva, L. M. P. F. Amaral, P. Jiménez, M. V. Roux, J. Z. Dávalos, M. Temprado, P. Cabildo, R. Claramunt, J. Elguero, O. Mó and M. Yáñez, J. Chem. Thermodyn., 36 (2004) 533.
24 P. Jiménez, M. V. Roux, J. Z. Dávalos, M. Temprado, M. A. V. Ribeiro da Silva, M. D. M. C. Ribeiro da Silva, L. M. P. F. Amaral, P. Cabildo, R. Claramunt, O. Mó, M. Yáñez and J. Elguero, Mol. Phys., 102 (2004) 711.
25 M. A. V. Ribeiro da Silva, M. D. M. C. Ribeiro da Silva, L. M. P. F. Amaral, J. Elguero, P. Jimenez, M. V. Roux, J. Z. Dávalos, M. Temprado, P. Cabildo, R. Claramunt, O. Mó and M. Yáñes, J. Chem. Thermodyn., 37 (2005) 1168.
26 M. A. V. Ribeiro da Silva, C. P. F. Santos, M. J. S. Monte and C. A. D. Sousa, J. Therm. Anal. Cal., 83 (2006) 533.
27 M. A. V. Ribeiro da Silva and C. P. F. Santos, J. Therm. Anal. Cal., 87 (2006) 21.
28 M. A. V. Ribeiro da Silva, V. M. A. R. Morais, M. A. R. Matos, C. M. A. Rio and C. M. G. S. Piedade, Struct. Chem., 7 (1996) 329.
29 M. A. V. Ribeiro da Silva and J. I. T. A. Cabral, J. Chem. Thermodyn., 38 (2006) 1461.
30 M. A. V. Ribeiro da Silva and J. I. T. A. Cabral, J. Chem. Eng. Data, 51 (2006) 1556.
31 M. A. V. Ribeiro da Silva, J. I. T. A. Cabral and J. R. B. Gomes, J. Chem. Thermodyn., 38 (2006) 1072.
32 M. A. V. Ribeiro da Silva and J. I. T. A. Cabral, J. Chem. Thermodyn., 38 (2006) 1008.
33 M. A. V. Ribeiro da Silva, J. I. T. A. Cabral, P. Gomes and J. R. B. Gomes, J. Org. Chem., 71 (2006) 3677.
34 M. A. V. Ribeiro da Silva and J. I. T. A. Cabral, J. Chem. Eng. Data, 51 (2006) 767.
35 M A. V. Ribeiro da Silva and J. I. T. A. Cabral, Thermochim. Acta, 453 (2006) 147.
36 M. A. V. Ribeiro da Silva, M. D. M. C. Ribeiro da Silva and G. Pilcher, Rev. Por. Quím., 26 (1984) 163.
37 M. A. V. Ribeiro da Silva, M. D. M. C. Ribeiro da Silva and G. Pilcher, J. Chem. Thermodyn., 16 (1984) 1149.
38 Certificate of Analysis Standard Reference Material 39j Benzoic Acid Calorimetric Standard. NBS, Washington (1995).
39 J. Copps, R. S. Jessup and K. Van Nes, in: F. D. Rossini, (Ed.), Experimental Thermochemistry, Vol. 1, Interscience, New York 1956, Chapter 3.
40 M. A. V. Ribeiro da Silva, M. A. R. Matos and L. M. P. F. Amaral, J. Chem. Thermodyn., 27 (1995) 565.
41 F. A. Adedeji, D. L. S. Brown and J. A. Connor, M. Leung, M. I. Paz-Andrade and H. A. Skinner, J. Organomet. Chem., 97 (1975) 221.

42 L. M. N. B. F. Santos, B. Schröder, O. O. P. Fernandes and M. A. V. Ribeiro da Silva, Thermochim. Acta, 415 (2004) 15.
43 R. Sabbah, A. Xu-Wu, J. D. Chickos, M. L. Planas Leitão, M. V. Roux and L. A. Torres, Thermochim. Acta, 331 (1999) 93.
44 R. D. Stull, E. F. Westrum and G. C. Sinke, The Chemical Thermodynamics of Organic Compounds, Wiley, New York 1969.
45 W. N. Hubbard, D. W. Scott and G. Waddington, in F. D. Rossini (Ed.), Experimental Thermochemistry, Vol. 1, Interscience: New York 1956, Chapter 5.
46 H. A. Skinner and A. Snelson, Trans. Faraday Soc., 56 (1960) 1776.
47 D. D. Wagmar; W. H. Evans, V. B. Parker, R. H. Shum, F. Halow, S. M. Bailey, K. L. Churney and R. L. Nuttall, J. Phys. Chem., Ref. Data 11, Suppl. 2 (1982).
48 J. D. Cox, D. D. Wagman and V. A. Medvedev, CODATA Key Values for Thermodynamics, Hemisphere, New York 1989.
49 E. N. Washburn, J. Res. Natl. Bur. Stand. (USA), 10 (1933) 525.
50 R. D. Loss, Pure Appl. Chem., 35 (2003) 1107.
51 F. D. Rossini, in: F. D. Rossini (Ed.) Experimental Thermochemistry, Vol. 1, Interscience, New York 1956, Chapter 14.
52 G. Olofsson, in: S. Sunner and M. Månsson (Eds) Combustion Calorimetry; Pergamon, Oxford 1979, Chapter 6.
53 J. F. Messerly, S. S. Todd, H. L. Fink, W. D. Good and B. E. Gammon, J. Chem. Thermodyn., 20 (1988) 209.
54 S. P. Verevkin, J. Chem. Thermodyn., 22 (1990) 893.
55 W. Good, J. Chem. Eng. Data, 17 (1972) 28.
56 E. J. Prosen, W. H. Johnson and F. D. Rossini, J. Res. Natl. Bur. Stand., 37 (1946) 51.
57 S. P. Verevkin, Struct. Chem., 9 (1998) 113.

Received: January 3, 2007
Accepted: October 12, 2007

DOI: 10.1007/s10973-007-8316-0