



Enthalpies of combustion, heat capacities, and enthalpies of vaporization of 1-ethylimidazole and 1-ethylpyrazole

Manuel A. V. Ribeiro da Silva, ^a Maria das Dores M. C. Ribeiro da Silva, M. Agostinha R. Matos,

Centro de Investigação em Química, Department of Chemistry, Faculty of Science, University of Porto, Rua do Campo Alegre, 687, P-4150 Porto, Portugal

Pilar Jimenez, M. Victoria Roux,

Instituto de Química Física "Rocasolano", C.S.I.C., Serrano 119, 28006 Madrid, Spain

José Elguero,

Instituto de Química Médica, C.S.I.C., Juan de la Cierva, 3, 28006 Madrid, Spain

Rosa Claramunt, Pilar Cabildo,

Departamento de Química Orgánica y Biología, Facultad de Ciencias, UNED, 28040 Madrid, Spain

and Ana Sanchez-Migallón

Facultad de Química, Universidad de Castilla- La Mancha, 13071 Ciudad Real, Spain

The standard ($p^{\circ} = 0.1 \text{ MPa}$) molar enthalpies of formation for liquid 1-ethylimidazole and 1-ethylpyrazole were derived from the standard molar enthalpies of combustion $\Delta_c H_m^{\circ}$, in oxygen, at T = 298.15 K, measured by static bomb combustion calorimetry. The molar heat capacities of both liquids were measured in the temperature range (280 to 365) K by differential scanning calorimetry. The standard molar enthalpies of vaporization $\Delta_g^g H_m^{\circ}$, at the temperature T = 298.15 K were measured by Calvet microcalorimetry. The derived standard molar enthalpies of formation in the gaseous state are compared.

	$-\Delta_{\rm c} H_{\rm m}^{\circ}({\rm l})/({\rm kJ}\cdot{\rm mol}^{-1})$	$\Delta_{\rm l}^{\rm g} H_{\rm m}^{\circ}/({\rm kJ}\cdot{\rm mol}^{-1})$
1-Ethylimidazole	3155.7 ± 4.7	66.0 ± 3.9
1-Ethylpyrazole	3190.2 ± 2.1	53.3 ± 2.4

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KEYWORDS: enthalpies of combustion; enthalpies of formation; enthalpies of vaporization; 1-ethylimidazole; 1-ethylpyrazole; heat capacities

^a To whom correspondence should be adressed (E-mail: risilva@fc.up.pt).



FIGURE 1. Molecular structure of a, 1-ethylimidazole, and b, 1-ethylpyrazole.

1. Introduction

The thermochemical study of heterocyclic molecules has interested our research centres for the last few years.⁽¹⁻²¹⁾ Some attention has been given to the study of azoles, and their alkyl and aryl substituted carbon derivatives.⁽¹⁻⁴⁾ In this work we begin the thermochemical study of *N*-substituted derivatives of imidazole and pyrazole.

This paper reports the standard ($p^{\circ} = 0.1$ MPa) molar enthalpies of combustion, in oxygen, at the temperature 298.15 K, measured by static bomb combustion calorimetry, for the liquid 1-ethylimidazole and 1-ethylpyrazole (figure 1).

The standard molar enthalpies of vaporization were determined by Calvet microcalorimetry. Heat capacities were determined by using d.s.c. The derived values for the standard molar enthalpies of formation for the compounds in the gaseous state are analysed.

These compounds were selected as part of a multistep approach to the study of the effect of *N*-substituents on the properties of aromatic compounds. This study was undertaken to gain information on two related questions: how substituent effects are transmitted through the nitrogen, and how the aromaticity of imidazole and pyrazole rings is affected by *N*-substituents.⁽²²⁾ Concerning the first point, knowledge about transmission of substituent effects is restricted to *C*-substituents (benzene and other aromatic rings including *C*-substituted heterocycles).⁽²²⁻²⁴⁾ Regarding the second point, the only available information concerns the parent compounds, imidazole and pyrazole themselves.⁽²⁵⁻³⁰⁾ Concerning the geometry of these compounds, we have previously shown that angular deformations which affect the endocyclic angles in pyrazoles (N1) and in benzenes (*Cipso*) are linearly related.⁽³¹⁾

2. Experimental

The 1-ethylimidazole⁽³²⁾ was prepared by mixing imidazole (10 mmol), potassium *tert*-butoxide (11 mmol), and *tetra-n*-butylammonium bromide (TBAB, 0.5 mmol),

and submerging in an ultrasonic cleaning bath (50 W, 200 MHz) for 15 min. Ethyl iodide (10 mmol) was added at T = 273 K and the reaction mixture was subjected to ultrasound for 3 h. The mixture was extracted with dichloromethane (two portions of 15 cm³). After removal of the solvent and *tert*-butanol, the product was distilled twice over sodium in a nitrogen atmosphere in a Vigreux column, giving a yield of 80 per cent of a product with boiling temperature $T_b = 378$ K at $p = 19 \cdot 10^3$ Pa. Literature values⁽³³⁾ are $T_b = 481$ K at $p = 1.01 \cdot 10^5$ Pa.

The 1-ethylpyrazole⁽³²⁾ was prepared by reacting pyrazole (10 mmol), finely ground potassium hydroxide (20 mmol), and TBAB (0.5 mmol) in an ultrasonic bath for 15 min. Ethyl iodide (10 mmol) was added at T = 273 K and the reaction mixture was subjected to ultrasound for 24 h. The mixture was extracted with dichloromethane (two portions of 15 cm³), and the product was distilled twice over sodium in a nitrogen atmosphere in a Vigreux column. The yield was 85 per cent, with a boiling temperature $T_{\rm b} = 343$ K at $p = 19 \cdot 10^3$ Pa. Literature values are $T_{\rm b} = (409 \text{ to } 410)$ K at $p = 9.95 \cdot 10^4$ Pa,⁽³³⁾ and $T_{\rm b} = 409$ K at $p = 1.01 \cdot 10^5$ Pa.^(34,35) Purities were checked by C, H, N elemental analysis.

Both 1-ethylimidazole and 1-ethylpyrazole are hygroscopic liquids. Although the handling of samples was performed under nitrogen, the average ratios of the mass of carbon dioxide recovered after combustion to that calculated from the mass of sample were: for 1-ethylimidazole (0.9980 \pm 0.0006), and for 1-ethylpyrazole (0.9955 \pm 0.0007), where the uncertainties are the standard deviation of the mean.

The combustion experiments were performed with a static bomb calorimeter, and the apparatus and technique have been described.⁽³⁶⁾ Benzoic acid (Bureau of Analysed Samples, Thermochemical Standard, BCS-CRM-190 p) was used for calibration of the bomb. Its massic energy of combustion is $-(26431.8 \pm 3.7) \text{ J} \cdot \text{g}^{-1}$ under certificate conditions. The calibration results were corrected to give the energy equivalent ε (calor) corresponding to the average mass of water added to the calorimeter, 3119.6 g. From eight calibration experiments, ε (calor) = (15911.2 ± 1.5) J·K⁻¹, where the uncertainty quoted is the standard deviation of the mean. For all experiments, ignition was made at $T = (298.150 \pm 0.001)$ K. Combustion experiments were performed in oxygen at p = 3.04 MPa, with 1 cm³ of water added to the bomb. The liquid 1-ethylimidazole and 1-ethylpyrazole were burnt in sealed polyester bags (Melinex) by using the technique described by Skinner and Snelson,⁽³⁷⁾ who determined the specific energy of combustion of dry Melinex as $\Delta_c u^\circ = -(22902 \pm 5) \, \text{J} \cdot \text{g}^{-1}$. That value was confirmed in the Porto laboratory. The mass of Melinex used in each experiment was corrected for the mass fraction of water (0.0032), and the mass of carbon dioxide produced from it was calculated by using the factor previously reported.⁽³⁷⁾ The electrical energy for ignition was determined from the change in potential difference across a capacitor when discharged through the platinum ignition wire. For the cotton-thread fuse, empirical formula $CH_{1.686}O_{0.843}$, $\Delta_c u^{\circ} = -16250 \text{ J} \cdot \text{g}^{-1}$.⁽³⁸⁾ The corrections for nitric acid formation were based on $-59.7 \text{ kJ} \cdot \text{mol}^{-1(39)}$ for the molar energy of formation of $0.1 \text{ mol} \cdot \text{dm}^{-3}$ HNO₃(aq) from N₂, O₂, and H₂O(l).

The amount of substance used in each experiment was determined from the total mass of carbon dioxide produced after allowance was made for that formed

from the cotton thread fuse and Melinex. The densities at T = 298.15 K for both 1-ethylimidazole and 1-ethylpyrazole were measured by using an Anton Paar DMA 02D densimeter, as $0.959 \,\mathrm{g}\cdot\mathrm{cm}^{-3}$ and $1.08 \,\mathrm{g}\cdot\mathrm{cm}^{-3}$. An estimated pressure coefficient of massic energy, $(\partial u / \partial p)_T = -0.2 \,\mathrm{J}\cdot\mathrm{g}^{-1}\cdot\mathrm{MPa}^{-1}$ at T = 298.15 K, a typical value for most organic compounds, was assumed. For each compound, the massic energy of combustion $\Delta_c u^\circ$ was calculated by the procedure given by Hubbard *et al.*⁽⁴⁰⁾

A differential scanning calorimeter (Perkin-Elmer DSC-2C), connected to a Model 3600 Data Station and equipped with an Intracooler-2-unit, was used in this research. Its temperature and power scales were calibrated by measuring the melting temperatures of the usual high-purity reference materials: *n*-octadecane, *n*-octadecanoic acid, benzoic acid, and indium. The power scale was calibrated by using high-purity indium (x > 0.99999) as reference material.⁽⁴¹⁾

Heat capacities were calculated by means of the heat-capacity programme. Synthetic sapphire and benzoic acid were used as standard materials⁽⁴²⁾ for checking all the procedures. The complete temperature range for determination of the heat capacities was divided into three intervals of approximately 40 K, overlapping by 15 K from one interval to another. The heat capacity values were the average of four experiments performed for each interval of temperature. Fresh samples of mass 8 mg were scanned using a heating rate of $0.17 \,\mathrm{K} \cdot \mathrm{s}^{-1}$ and a sensitivity of 0.008 W full scale. All the samples were handled under a nitrogen atmosphere. The estimated error of the molar heat capacities was between $0.01 \cdot C_{p,m}$ and $0.02 \cdot C_{p,m}$.

The enthalpies of vaporization of 1-ethylimidazole and 1-ethylpyrazole were measured by using a method similar to that used for sublimation of solids, the "vacuum sublimation" drop microcalorimetric method,⁽⁴³⁾ which was previously tested in the Porto laboratory.⁽⁹⁾ Samples of about (7 to 11) mg of each liquid compound, contained in a thin glass capillary tube sealed at one end, were dropped, at room temperature, into the hot reaction vessel in a high-temperature Calvet microcalorimeter held at T = 371 K (1-ethylimidazole) and T = 373 K (1ethylpyrazole), and then removed from the hot zone by vacuum vaporization. The observed enthalpies of vaporization were corrected to T = 298.15 K by using the value of $\int_{298.15 \text{ K}}^{T} C_{p,m}^{\circ}(g) dT$ estimated by the Benson group method,⁽⁴⁴⁾ with values from Stull *et al.*⁽⁴⁵⁾ The microcalorimeter was calibrated *in situ* for these measurements by using the reported enthalpy of vaporization of undecane.⁽⁴⁶⁾ The molar masses used for the elements were those recommended by IUPAC in 1993.⁽⁴⁷⁾

The geometries of imidazole and pyrazole, as well as those of their 1-ethyl derivatives, were optimized at the B3LYP/6-31G (d,p) level, which was shown to yield quite reliable geometries for this kind of system.⁽⁴⁸⁾ For the 1-ethyl derivatives, we have initially considered two alternative conformers, **EI1** (1-ethylimidazole 1), **EI2** (1-ethylimidazole 2), **EP1** (1-ethylpyrazole 1), and **EP2** (1-ethylpyrazole 2), which differ in the relative positions of the methyl group of the ethyl substituent with respect to the azole ring (see figure 2).

In all cases, both conformers evolve to yield a sole equilibrium conformation, **EI** and **EP**, respectively, in which the methyl group is located in a plane almost



FIGURE 2. Conformers of 1-ethylimidazole (ET1 and ET2), and of 1-ethylpyrazole (EP1 and EP2).

perpendicular to the plane of the azole ring (figure 2). The harmonic vibrational frequencies were evaluated at the same level of theory. This allows us both to confirm that the stationary points found correspond to local minima of the corresponding potential energy surfaces, and to evaluate the zero-point energy (ZPE) corrections, which were scaled by the empirical factor 0.98.⁽⁴⁹⁾

To have reliable energetics, the final total energies of these systems were obtained in single-point calculations at the B3LYP/6-311 + G(3df,2p) level, which usually yields thermodynamic properties, such as proton affinities, or enthalpies of formation, in fairly good agreement with those obtained from the G2-theory, which is prohibitively expensive for systems of this size.

3. Results

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, and ΔU_{Σ} is the correction to the standard state. The remaining

	1-Ethylimidazole	1-Ethylpyrazole	
$\overline{m(CO_2)/g}$	1.76867	1.47980	
m'(cpd)/g	0.69893	0.59327	
m'' (Melinex)/g	0.07121	0.05045	
m'''(fuse)/g	0.00353	0.00385	
$\Delta T_{\rm ad}/{\rm K}$	1.55103	1.31586	
$\varepsilon_{\rm f}/({\rm J}\cdot{\rm K}^{-1})$	16.20	15.89	
$\Delta m(H_2O)/g$	-0.2	0.3	
$-\Delta U(\tilde{IBP})/\tilde{J}^{a}$	24701.92	20958.37	
$\Delta U(HNO_3)/J$	68.66	56.73	
$\Delta U(\text{ign.})/J$	0.66	1.10	
$\Delta U_{\Sigma} / \mathbf{J}$	14.57	11.98	
ΔU (Melinex)/J	1630.89	1155.49	
$\Delta U(\text{fuse})/\text{J}$	57.33	62.52	
$-\Delta_{c} u^{\circ} / (\mathbf{J} \cdot \mathbf{g}^{-1})$	32807.96	33158.01	

TABLE 1. Results of typical combustion experiments for 1-ethylimidazole and 1-ethylpyrazole at $T=298.15\,{\rm K}$

^{*a*} ΔU (IBP) already includes the ΔU (ign.).

$-\Delta_{\rm c} u^{\circ}/({\rm J}\cdot{\rm g}^{-1})$					
1-Ethylimidazole	1-Ethylpyrazole				
32818.07	33138.25				
32767.97	33127.03				
32842.10	33159.23				
32807.96	33191.76				
32803.13	33158.01				
32795.90	33183.70				
32787.64					
32782.19					
$-\langle \Delta_{\rm c} u^{\circ} \rangle / ({f J} \cdot {f g}^{-1})^a$					
32800.6 ± 8.0	33159.7 ± 10.2				

TABLE 2. Individual values of the massic energy of combustion $\Delta_c u^o$ of 1-ethylimidazole and 1-ethylpyrazole at T = 298.15 K

^a Mean value and standard deviation of the mean.

quantities are as previously described.⁽⁴⁰⁾ As samples were ignited at T = 298.15 K,

$$\Delta U(\text{IBP}) = -\{\varepsilon_{\text{(calor)}} + \Delta n_{\text{(t)}} H_2 O : c_{\text{(p)}} H_2 O, | t + \varepsilon_f\} \Delta T_{\text{ad}} + \Delta U_{\text{igh}} . \right) 1$$

The individual results of all combustion experiments, together with the mean value and its standard deviation, are given for each compound in table 2. Table 3 lists the derived standard molar energies and enthalpies of combustion, $\Delta_c U_m^{\circ}(l)$ and $\Delta_c H_m^{\circ}(l)$, respectively, and the standard molar enthalpies of formation $\Delta_f H_m^{\circ}(l)$ for the two liquid compounds at T = 298.15 K. In accordance with normal thermochemical practice, the uncertainties assigned to the standard molar enthalpies of combustion are, in each case, twice the overall standard deviation of the mean, and include the uncertainties in calibration⁽⁵⁰⁾ and in the values of auxiliary quantities. To derive $\Delta_f H_m^{\circ}(l)$ from $\Delta_c H_m^{\circ}(l)$ the standard molar enthalpies of formation of H₂O(l) and CO₂(g) at T = 298.15 K, $-(285.830 \pm 0.042)$ kJ·mol⁻¹⁽⁵¹⁾ and $-(393.51 \pm 0.13)$ kJ·mol^{-1,(51)} respectively, were used.

The molar heat capacities for the liquid 1-ethylimidazole and 1-ethylpyrazole were measured from T = 280 K to the temperature of vaporization; the temperatures were corrected by a programme that includes the calibrations of temperature and power scales of the d.s.c. apparatus, and values of $C_{p,m}$ are given in table 4.

TABLE 3. Derived standard ($p^{\circ} = 0.1 \text{ MPa}$) molar energies of combustion $\Delta_c U_m^{\circ}$, standard molar enthalpies of combustion $\Delta_c H_m^{\circ}$, and standard molar enthalpies of formation $\Delta_f H_m^{\circ}$ for 1-ethylimidazole and 1-ethylpyrazole at T = 298.15 K

	$-\Delta_{\rm c} U_{\rm m}^{\circ}({\rm l})/({\rm kJ}\cdot{ m mol}^{-1})$	$-\Delta_{\rm c} H_{\rm m}^{\circ}({\rm l})/({\rm kJ}\cdot{\rm mol}^{-1})$	$\Delta_{\rm f} H_{\rm m}^{\circ}({\rm l})/({\rm kJ}\cdot{\rm mol}^{-1})$
1-Ethylimidazole 1-Ethylpyrazole	$\begin{array}{c} 3153.2\pm1.7\\ 3187.7\pm2.1 \end{array}$	$\begin{array}{c} 3155.7\pm1.7\\ 3190.2\pm2.1 \end{array}$	$\begin{array}{c} 44.8\pm1.8\\ 79.3\pm2.2\end{array}$

T/\mathbf{K}	$C_{p,\mathbf{m}}/(\mathbf{J}\cdot\mathbf{K}^{-1}\cdot\mathbf{mol}^{-1})$	T/K	$C_{p, \mathbf{m}}/(\mathbf{J}\cdot\mathbf{K}^{-1}\cdot\mathbf{mol}^{-1})$	T/K	$C_{p,\mathrm{m}}/(\mathrm{J}\cdot\mathrm{K}^{-1}\cdot\mathrm{mol}^{-1})$
			1-ethylimidazole		
280.1	180.99	310.4	188.45	340.4	200.53
285.2	183.96	315.4	190.66	345.4	202.66
290.2	183.53	320.4	192.63	350.3	203.21
295.3	186.16	325.4	194.99	355.3	205.84
303.3	187.48	330.4	198.17	359.2	207.48
305.4	188.20	335.4	202.03	365.2	211.80
			1-ethylpyrazole		
280.3	170.90	310.5	195.55	340.5	216.62
285.3	177.76	315.5	196.35	345.5	218.19
290.4	179.95	320.5	199.45	350.4	217.09
295.4	185.37	325.5	204.28	355.4	224.90
300.4	192.26	330.5	208.35	360.4	227.27
305.4	195.27	335.5	215.61	365.4	233.87

TABLE 4. Experimental molar heat capacities $C_{p,\,\rm m}$ of 1-ethylimidazole and 1-ethylpyrazole in the liquid state

TABLE 5. Standard ($p^{\circ} = 0.1 \text{ MPa}$) molar enthalpies of vaporization $\Delta_{\Gamma}^{g \ T} H_{m}^{\circ}$ at various temperatures T for 1-ethylimidazole and 1-ethylpyrazole, determined by microcalorimetry

	No. of expts	T/K	$\frac{\Delta_{\mathrm{I}}^{\mathrm{g},T}H_{\mathrm{m}}^{\circ}}{\mathrm{kJ}\cdot\mathrm{mol}^{-1}}$	$\frac{\int_{298.15 \text{ K}}^{T} C_{p, \text{m}}^{\circ}(\mathbf{g}) \mathrm{d}T}{\mathrm{kJ} \cdot \mathrm{mol}^{-1}}$	$\frac{\Delta_{\rm I}^{\rm g}H_{\rm m}^{\circ}(298.15{\rm K})}{{\rm kJ}\cdot{\rm mol}^{-1}}$
1-Ethylimidazole 1-Ethylpyrazole	7 5	371 373	$\begin{array}{c} 75.6 \pm 3.9 \\ 63.2 \pm 2.4 \end{array}$	9.6 9.9	$\begin{array}{c} 66.0 \pm 3.9 \\ 53.3 \pm 2.4 \end{array}$

Values of the enthalpies of vaporization $\Delta_1^g H_m^{\circ}$ are given in table 5, with uncertainties of twice the standard deviation of the mean.

The derived enthalpies of formation in both the condensed and gaseous phases for 1-ethylimidazole and 1-ethylpyrazole are summarized in table 6.

4. Discussion

To discuss the enthalpies of formation of 1-ethylimidazole and 1-ethylpyrazole (table 6) we have first studied the imidazole–pyrazole pair. In a previous paper,⁽¹⁾ we have reported the following values for $\Delta_f H_m^{\circ}(g)$: pyrazole (179.4 \pm 0.8) kJ·mol⁻¹, and imidazole (132.9 \pm 0.6) kJ·mol⁻¹. Thus, of the two compounds of formula

TABLE 6. Derived standard ($p^{\circ} = 0.1 \text{ MPa}$) molar enthalpies of formation $\Delta_{\rm f} H^{\circ}_{\rm m}$ of 1-ethylimidazole and 1-ethylpyrazole at T = 298.15 K

	$\Delta_{\rm f} H_{\rm m}^{\circ}({\rm l})/({\rm kJ}\cdot{\rm mol}^{-1})$	$\Delta_{\rm I}^{\rm g} H_{\rm m}^{\circ}/({\rm kJ} \cdot {\rm mol}^{-1})$	$\Delta_{\rm f} H_{\rm m}^{\circ}({\rm g})/({\rm kJ}\cdot{\rm mol}^{-1})$
1-Ethylimidazole 1-Ethylpyrazole	$\begin{array}{c} 44.8\pm1.8\\ 79.3\pm2.2\end{array}$	$\begin{array}{c} 66.0 \pm 3.9 \\ 53.3 \pm 2.4 \end{array}$	$\begin{array}{c} 110.8 \pm 4.3 \\ 132.6 \pm 3.3 \end{array}$

Compound	$U^a/{{ m E}_{ m h}}^b$	$U^c/\mathrm{E_h}^b$	$U(T \rightarrow 0)/\mathrm{E_h}^b$	$\frac{\Delta U}{\mathbf{kJ}\cdot\mathbf{mol}^{-1}}^{d}$
Imidazole	-226.22309	-226.29940	0.07126	0.0
Pyrazole	-226.20703	-226.29870	0.07140	44.8
1-Ethylimidazole (EI)	-304.85577	-304.95039	0.12784	0.0
1-Ethylpyrazole (EP)	-304.84243	-304.93602	0.12783	33.7

TABLE 7. Total energies U, zero-point energies $U(T \rightarrow 0)$, and relative energies ΔU of imidazole, pyrazole, 1-ethylimidazole, and 1-ethylpyrazole

^{*a*} E_h = 2625.50 kJ. ^{*b*} B3LYP/6-31G(d,p). ^{*c*} B3LYP/6-311 + G(3df,2p)//B3LYP/6-31G(d,p). ^{*d*} These values include the corresponding corrections for $U(T \rightarrow 0)$.

 $C_3H_4N_2$, imidazole is more stable by $(46.5 \pm 1.0) \text{ kJ} \cdot \text{mol}^{-1}$. The results of the theoretical calculation, after ZPE correction, reported in table 7, is $44.8 \text{ kJ} \cdot \text{mol}^{-1}$. This excellent agreement encourages us to do the same kind of calculation for the 1-ethylimidazole–1-ethylpyrazole pair. The theoretical result, $33.7 \text{ kJ} \cdot \text{mol}^{-1}$, although showing a decrease in the difference in stability, is still far from the experimental value, $(21.8 \pm 5.4) \text{ kJ} \cdot \text{mol}^{-1}$, which is in line with that recently found by Curtiss *et al.*⁽⁵²⁾ for a large number of molecules, for which the mean absolute difference for calculated enthalpies of formation by B3LYP is $13 \text{ kJ} \cdot \text{mol}^{-1}$. Before going further from the preliminary conclusion that the differences in aromaticity between imidazoles and pyrazoles decrease from N–H to N-ethyl derivatives, it is necessary to study other pairs of *N*-substituted azoles, both experimentally and theoretically.

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REFERENCES

- 1. Jiménez, P.; Roux, M. V.; Turrion, C.; Gomis, F. J. Chem. Thermodynamics 1987, 19, 985-992.
- 2. Jiménez, P.; Roux, M. V.; Turrion, C. J. Chem. Thermodynamics 1989, 21, 759-764.
- 3. Jiménez, P.; Roux, M. V.; Turrion, C. J. Chem. Thermodynamics 1990, 22, 721-725.
- 4. Jiménez, P.; Roux, M. V.; Turrion, C. J. Chem. Thermodynamics 1992, 24, 1145-1149.
- Ribeiro da Silva, M. A. V.; Monte, M. J. S.; Matos, M. A. R. J. Chem. Thermodynamics 1989, 21, 159–166.
- Ribeiro da Silva, M. A. V.; Matos, M. A. R.; Monte, M. J. S. J. Chem. Thermodynamics 1990, 22, 609–616.
- 7. Ribeiro da Silva, M. A. V.; Monte, M. J. S. J. Chem. Thermodynamics 1992, 24, 715-724.
- Ribeiro da Silva, M. A. V.; Matos, M. A. R.; Monte, M. J. S.; Álves, M. C. B.; Vieira, J. M. A. P. J. Chem. Thermodynamics 1993, 25, 579–590.
- Ribeiro da Silva, M. A. V.; Matos, M. A. R.; Amaral, L. M. P. F. J. Chem. Thermodynamics 1995, 27, 565–574.
- Ribeiro da Silva, M. A. V.; Ferrão, M. L. C. C. H.; Silva, A. M. R. O. A. J. Chem. Thermodynamics 1995, 27, 633–641.

- 11. Ribeiro da Silva, M. A. V.; Matos, M. A. R.; Amaral, L. M. P. F. J. Chem. Thermodynamics **1995**, 27, 1141–145.
- 12. Ribeiro da Silva, M. A. V.; Matos, M. A. R.; Amaral, L. M. P. F. J. Chem. Thermodynamics **1995**, 27, 1187–1196.
- 13. Ribeiro da Silva, M. A. V.; Morais, V. M. F.; Matos, M. A. R.; Rio, C. M. A. J. Org. Chem. **1995**, 60, 5291–5294.
- 14. Ribeiro da Silva, M. A. V.; Morais, V. M. F.; Matos, M. A. R. J. Chem. Soc. Faraday Trans. 1995, 92, 1907–1910.
- Ribeiro da Silva, M. A. V.; Morais, V. M. F.; Matos, M. A. R.; Rio, C. M. A.; Piedade, C. M. G. S. Structural Chem. 1996, 7, 329–336.
- 16. Ribeiro da Silva, M. A. V.; Matos, M. A. R.; Pure & Applied Chemistry 1997, 69, 2295-2305.
- 17. Ribeiro da Silva, M. A. V.; Matos, M. A. R.; Rio, C. M. A. J. Chem. Thermodynamics 1997, 29, 901–906.
- Ribeiro da Silva, M. A. V.; Matos, M. A. R.; Amaral, L. M. P. F. J. Chem. Thermodynamics 1997, 29, 1129–1136.
- 19. Ribeiro da Silva, M. A. V.; Morais, V. M. F.; Matos, M. A. R.; Rio, C. M. A. J. Chem. Soc. Faraday Trans. 1997, 93, 3061–3065.
- 20. Ribeiro da Silva, M. A. V.; Matos, M. A. R.; Amaral, L. M. P. F. J. Chem. Thermodynamics **1997**, 29, 1535–1543.
- 21. Ribeiro da Silva, M. A. V.; Matos, M. A. R.; Amaral, L. M. P. F. J. Chem. Thermodynamics **1997**, 29, 1545–1551.
- Hammett, L. P. Physical Organic Chemistry. McGraw-Hill: New York. 1940; Chapman, N. B.; Shorter, J. Advances in Linear Free Energy Relationships. Plenum Press: London. 1972; Chapman, N. B.; Shorter, J. Correlation Analysis in Chemistry. Plenum Press: New York. 1978; Hansch, C.; Leo, A.; Taft, R. W. Chem. Rev. 1991, 91, 165; Hansch, C.; Leo, A., Hoekman, D. Exploring QSAR, Hydrophobic and Steric Constant. ACS Professional Reference Book. American Chemical Society: Washington, DC. 1995.
- 23. Decouzon, M.; Exner, O.; Gal, J. F.; Maria, P. C. J. Phys. Org. Chem. 1994, 7, 615-624.
- 24. Elguero, J.; Gil, M.; Iza, N.; Pardo, C., Ramos, M. Appl. Spectrosc. 1995, 49, 1111-1119.
- 25. Friedman, P.; Ferris, K. F. Int. J. Quantum. Chem. 1990, 24, 843-850.
- 26. Katritzky, A. R.; Barczynski, P.; Musumarra, G.; Pisano, D.; Szfran, M. J. Am. Chem. Soc. 1989, 111, 7–15.
- Katritzky, A. R.; Feygelman, V.; Musumarra, G.; Barczynski, P.; Szafran, M. J. Prakt. Chem. 1990, 332, 870–884.
- 28. Caruso, L.; Musumarra, G.; Katritsky, A. R. Quant. Struct.-Act. Relat. 1993, 12, 146-151.
- Bird, C. W. Tetrahedron 1985, 41, 1409–1414; Bird, C. W. Tetrahedron 1992, 48, 335–340; Bird, C. W. Tetrahedron 1996, 52, 9945–9952; Bird, C. W. Tetrahedron 1997, 53, 3319–3324.
- 30. Clementi, S.; Cruciani, G.; Fifi, P.; Riganelli, D.; Valigi, R.; Musumarra, G. Quant. Struct.-Act. Relat. 1996, 15, 108-120.
- 31. Mó, O.; Yáñez, M.; Llama-Saiz, A. L.; Foces-Foces, C.; Elguero, J. Tetrahedron 1995, 51, 7045-7062.
- 32. Diez-Barra, E.; de la Hoz, A.; Sanchez-Migallón, A.; Tejeda, T. Synth. Commun. 1993, 23, 1783-1786.
- Handbook of Chemistry and Physics: 70th edition. Weast, R. C.: editor. CRC Press Inc.: Cleveland, OH, U.S.A. 1989.
- 34. Elguero, J.; Jacquier, R.; Tien Duc, H. C. N. Bull Soc. Chem. Fr. 1966, 3727-3743.
- 35. Dou, H. J. M.; Elguero, J.; Espada, M.; Hassanaly, P. An. Quim. 1978, 74, 1137-1139.
- 36. Ribeiro da Silva, M. A. V.; Ribeiro da Silva, M. D. M. C.; Pilcher, G. J. Chem. Thermodynamics 1984, 16, 1149–1155.
- 37. Skinner, H. A.; Snelson, A. Trans. Faraday Soc. 1960, 56, 1176-1183.
- Coops, J.; Jessup, R. S.; Van Nes, K. Experimental Thermochemistry, Vol. 1. Rossini, F. D.: editor. Interscience: New York. 1956, Chap. 3.
- 39. The NBS Tables of Chemical Thermodynamics Properties. J. Phys. Chem. Ref. Data 1982.
- 40. Hubbard, W. N.; Scott, D. W.; Waddington, G. *Experimental Thermochemistry*, Vol. 1. Rossini, F. D.: editor. Interscience: New York. **1956**, Chap. 5.
- 41. The d.s.c. calibration data was obtained from: (i) *n*-octadecane, *NPL Certificate of Measurement CRM NO M 14-11*, Set of Ten Melting Points Standards, National Physical Laboratory, Teddington. **1980**; (ii) *n*-octadecanoic acid, López de La Fuente F. L., PhD. Thesis, Facultad de Ciencias Químicas, Universidad Complutense, Madrid. **1989**; (iii) benzoic acid, Serge, S.; Camerga, H. K. *Thermochim Acta* **1985**, 94, 17–31; (iv) indium and tin, standard material and melting points supplied by Perkin-Elmer.

- 42. Head, A. J.; Sabbah, R. Recommended Reference Materials for the Realization of Physicochemical Properties. Marsh, K. N.: editor. Blackwell: Oxford. **1987**, Chap. 9, pp. 219–319.
- 43. Adedeji, F. A.; Brown, D. L. S.; Connor, J. A.; Leung, M.; Paz-Andrade, M. I.; Skinner, H. A. J. Organometallic Chem. 1975, 97, 221–228.
- 44. Benson, S. W. Thermochemical Kinetics. Methods for the estimation of thermochemical data rate parameters: 2nd edition. Wiley: New York. 1976.
- 45. Stull, D. R.; Westrum, E. F.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*. Wiley: New York. **1969**.
- 46. Pedley, J. B. *Thermochemical Data and Structures of Organic Compounds*, Vol. I. TRC Data Series: College Station, TX. **1994**.
- 47. J. Phys. Chem. Ref. Data, 1993, 22, 1571-1584.
- 48. Llamas-Saiz, A. L.; Foces-Foces, C.; Mó, O.; Yáñez, M.; Elguero, J. J. Comput. Chem. 1995, 16, 263–272.
- 49. Rauhut, G.; Pulay, P. J. Phys. Chem. 1995, 99, 3093-3100.
- 50. Rossini, F. D. *Experimental Thermochemistry*, Vol. 1. Rossini, F. D.: editor. Interscience: New York. **1956**, Chap. 14, pp. 297–320.
- 51. J. Chem. Thermodynamics 1978, 10, 903-906.
- 52. Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. J. Chem. Phys. 1997, 106, 1063-1069.

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