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Enthalpies of Formation of *N*-Substituted Pyrazoles and Imidazoles

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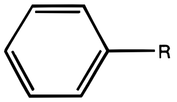
Accurate experimental enthalpies of formation measured using static bomb combustion calorimetry, the "vacuum sublimation" drop calorimetry method, and the Knudsen-effusion method are reported for the first time for four azoles: 1-methylimidazole (**1MeIMI**), 1-methylpyrazole (**1MePYR**), 1-benzylimidazole (**1BnIMI**), and 1-benzylpyrazole (**1BnPYR**). These values and those corresponding to imidazole (**1HIMI**), pyrazole (**1HPYR**), 1-ethylimidazole (**1EtIMI**), 1-ethylpyrazole (**1EtPYR**), 1-phenylimidazole (**1PhIMI**), and 1-phenylpyrazole (**1PhPYR**) are compared with theoretical values using the G2(MP2) and the B3LYP/6-311*G(3df,2p)//6-31G(d) approaches. In general, there is a very good agreement between calculated and experimental values for the series of *N*-substituted imidazoles, while the agreement is less good for the series of the *N*-substituted pyrazoles. Experimentally, the gap between the enthalpies of formation of imidazoles and pyrazoles decreases significantly upon *N*-substitution, while the theoretical estimates indicate that this decrease is smaller.

Introduction

The purpose of this work is to study the substituent effects through the nitrogen atom in diazoles (imidazoles and pyrazoles) comparatively to the effect of the same substituents through the carbon atom in benzenes. If benzenes **1** are the paradigm of an aromatic molecules, azoles are the simplest representatives of stable aromatic structures bearing *N*-substituents. Pyrroles being rather unstable compounds, *N*-substituted imidazoles **2** and pyrazoles **3** were selected.



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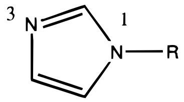

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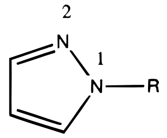

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The selected approach is a combination of experimental determinations and high-level ab initio calculations of enthalpies of formation. The five R groups are H, CH_3 (**Me**, methyl), C_2H_5 (**Et**, ethyl), $CH_2C_6H_5$ (**Bn**, benzyl), and C_6H_5 (**Ph**, phenyl). They correspond to the more important classes of substituents: aliphatic (methyl and ethyl), benzylic, and aromatic.

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Experimental Section

The heats of formation of the *N*-unsubstituted pairs (**1HIMI** and **1HPYR**) were already known when we started this study.[1] Those of the *N*-ethyl pairs (**1EtIMI** and **1EtPYR**) and *N*-phenyl pairs (**1PhIMI** and **1PhPYR**) have been published[2] or are in press.[3] The results concerning the remaining four compounds are described below.

Synthesis and Purity Control. *N*-Methylimidazole (**1MeIMI**) is a commercial product (Aldrich 33,609-2, purity > 99%, water < 0.03%). It was redistilled twice over freshly prepared sodium wire (in the following procedures, sodium always means freshly prepared sodium wire) in an argon atmosphere (bp = 471 K/760 mmHg). *N*-Methylpyrazole (**1MePYR**) was prepared using two different procedures. The first one proceeds by mixing pyrazole (20.4 g, 0.30 mol) and methyl iodide (20.6 g, 0.15 mol). The mixture was stirred at 323 K during 2 h. After that, to purify the residue was distilled twice using a Büchi Glass Oven model B-580 (390-400 K/760 mmHg) giving a final yield of 80% of a colorless product with boiling temperature bp = 397 K/760 mmHg. The second procedure uses phase transfer catalysis without solvent conditions; pyrazole (0.07 mol), finely grounded potassium hydroxide (0.14 mol), and tetra-*n*-butylammonium bromide (TBAB, 35 × 10^{-4} mol), were sonicated with an ultrasonic cleaning bath (50 W, 200 MHz) for 15 min. Methyl iodide (0.07 mol) was added at 273 K, and the reaction was stirred for 6 h. Distillation of reaction crude afforded a mixture of water and **1MePYR**. After removal of water, the product was dried over sodium hydroxide and distilled twice at 760 mmHg over sodium in an argon atmosphere using a Vigreux column (bp = 398−403 K): yield 80%; bp = 401 K/760 mmHg; lit. bp = 398 K/760 mmHg.[4] *N*-Benzylimidazole (**1BnIMI**) was prepared using the second procedure; imidazole (0.07 mol), potassium *tert*-butoxide (0.077 mol), and tetra-*n*-butylammonium bromide (TBAB, 35 × 10^{-4} mol) were mixed and submerged in an ultrasonic cleaning bath (50 W, 200 MHz) for 15 min. Benzyl chloride (0.07 mol) was added at 273 K, and the reaction was stirred at room temperature for 1 h. The mixture was extracted with dichloromethane (2 × 30 cm^3). After removal of the solvent, the product was distilled three times over sodium in an argon atmosphere using a Vigreux column (fraction 390−400 K/0.7 mmHg): yield 85%; bp = 395 K/0.7 mmHg; mp = 346 K; lit. mp = 345 K.[5] *N*-Benzylpyrazole (**1BnPYR**) was prepared analogously; pyrazole (0.07 mol), finely grounded potassium hydroxide (0,084 mol), and tetra-*n*-butylammonium bromide (TBAB, 35 × 10^{-4} mol) were sonicated with an ultrasonic bath for 15 min. Benzyl chloride (0.07 mol) was added at 273 K, and the reaction was stirred at room temperature for 48 h. The mixture was extracted with dichloromethane (2 × 30 cm^3). After removal of solvent, the product was distilled two times over sodium in an argon atmosphere using a Vigreux column: yield 90%; bp = 378 K/8 mmHg; lit. bp = 393 K/15 mmHg.[6]

Determination of purity was assessed by GC for the liquid compounds and by DSC using the fractional fusion technique for solid **1BnIMI**.[7] The mass fraction of impurities for the four compounds was 5 × 10^{-3}. 1-Benzylimidazole was studied by DSC over the temperature range between $T = 270$ K and $T = 349$ K and no phase transitions was found.

1MeIMI, **1MePYR**, and **1BnPYR** 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 **1MeIMI** (0.9969 ± 0.0006), **1MePYR** (0.9928 ± 0.0014), and **1BnPYR** (0.9996 ± 0.0002), where the uncertainties are the standard deviation of the mean. **1BnIMI** is a hygroscopic solid, and frequent NMR analyses were made in order to confirm the sample did not contain water.

Calorimetry. The combustion experiments were performed with two static bomb calorimeters I and II from Porto and Madrid, respectively. The apparatus and procedure have been described.[8] Benzoic acid (Bureau of Analysed Samples, Thermochemical Standard, BCS-CRM-190 p and BCS-CRM-190 c) were used for calibration of calorimeter I. Their specific energies of combustion are (26431.8 ± 3.7) J g^{-1} and (26432.3 ± 3.8) J g^{-1}, respectively, 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} was used for 1-methylimidazole and also from eight calibration experiments ϵ(calor) = (15908.3 ± 1.0) J K^{-1} was used for 1-methylpyrazole and 1-benzylpyrazole where the uncertainties quoted are the standard deviations of the means. For all experiments, ignition was made at $T = (298.150 \pm 0.001)$ K. Combustion experiments were made in oxygen at 3.04 MPa, with 1 cm^3 of water added to the bomb. The liquids **1MeIMI**, **1MePYR**, and **1BnPYR** were burnt in sealed polyester bags made of Melinex, using the technique described by Skinner and Snelson,[9] who determined the specific energy of combustion of dry Melinex as $\Delta_c u° = -(22902 \pm 5)$ J g^{-1}. That value was confirmed in Porto laboratory. The mass of Melinex used in each experiment was corrected for the mass of water (0.0032), and the mass of carbon dioxide produced from it was calculated using the factor previously reported.[9] 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, the empirical formula $CH_{1.686}O_{0.843}$,[10] $\Delta_c u° = 16\,250$ J g^{-1}, was used and the value of $\Delta_c u°$ confirmed. The amount of substance used in each experiment was determined from the total mass of carbon dioxide produced after allowance for that formed from the cotton thread fuse and Melinex.

The energy equivalent of the calorimeter II was determined from the combustion of benzoic acid, NIST standard reference sample 39i, having a massic energy of combustion under the conditions specified on the certificate of −(26434 ± 3) J g^{-1}. From 10 calibration experiments, ϵ(calor) = (14316.9 ± 2.0) J K^{-1}, where the uncertainty quoted is the standard deviation of the mean. The energy of combustion of the 1-benzylimidazole was determined by burning the solid sample in pellet form in oxygen inside the bomb, with 1 cm^3 of added water. As a result of the relatively high vapor pressure of **1BnIMI** and its hygroscopicity, the pelleted compound was enclosed in polyethene bags. Under these conditions no carbon or CO were found. The initial temperature was 296.95 K. The energy of reaction was always referred to the final temperature $T = 298.15$ K. The massic energy of combustion and empirical formula of polyethene are −(46371 ± 4) J g^{-1} and $C_{0.961}H_{2.000}$.[1] All samples were weighed with a Mettler AT-21 microbalance and corrections of apparent mass to mass were made. After disassembly of the calorimeter, the bomb gases were slowly released and the absence of CO was checked with Dräger tubes (sensitivity levels were approximately 1 × 10^{-6} mass fraction).

The corrections for nitric acid formation were based on −59.7 kJ mol^{-1} for the molar energy of formation of 0.1 mol dm^{-3} HNO_3(aq) from N_2(g), O_2(g), and H_2O(l).[11]

The densities at $T = 298.15$ K for **1MeIMI**, **1MePYR**, and **1BnPYR** were measured using an Anton Paar DMA 02D densimeter, respectively, as 1.030 g cm^{-3}, 0.9929 g cm^{-3}, and 1.078 g cm^{-3}. The density of **1BnIMI** was measured with a calibrated pycnometer $d = 1.22$ g cm^{-3}. An estimated pressure coefficient of specific energy, $(\delta u/\delta p)_T = -0.2$ J g^{-1} MPa^{-1} at $T = 298.15$ K, a typical value for most organic compounds, was assumed. For each compound, the massic energy of combustion, $\Delta_c u°$, was calculated by the procedure given by Hubbard et al.[12]

A differential scanning calorimeter (Perkin-Elmer Pyris 1) equipped with an Intracooler unit was used in this research in order to measure the heat capacities of all the compounds as well as to control the purity of solid **1BnIMI**. Its temperature scale was calibrated by measuring the melting temperature of the recommended high-purity reference materials: *n*-octadecane, octadecanoic acid, benzoic acid, tin, and indium.[13] The power scale was calibrated with high-purity indium (mass fraction: >0.99999) as reference material.[13]

Heat capacities were calculated following the method described in ref 14. Synthetic sapphire and benzoic acid were used as standard materials[15] for checking all the process. 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 done for each interval of temperature. Fresh samples of mass of approximately 8−12 mg were scanned using a heating rate of 0.17 K s^{-1} and a sensitivity of 0.008 W full scale. All the samples were handled under nitrogen atmosphere. The accuracy of the molar heat capacities was between 0.01 and 0.02 $C_{p,m}$ and the standard deviations of the mean of the experimental results were ±0.07 for **1MeIMI**, ±0.09 for **1MePYR**, ±0.10 for **1BnIMI**, and ±0.06 for **1BnPYR**.

The enthalpies of vaporization of **1MeIMI**, **1MePYR**, and **1BnPYR** were measured using a method similar to that used for sublimation of solids, the "*vacuum sublimation*" drop microcalorimetric method[16] which was previously tested in the Porto laboratory.[17] Samples, about 7−11 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 (**1MeIMI**), 363 K (**1MePYR**), and 386 K (**1BnPYR**) and then removed from the hot zone by vacuum vaporization. The observed enthalpies of vaporization were corrected to $T = 298.15$ K, using the value of

$$\int_{298.15\text{K}}^{T_o} C^\circ_{p,m}(g)\,dT$$

estimated by the Benson's group method,[18] using values from Stull et al.[19] The microcalorimeter was calibrated in situ for these measurements using the reported enthalpy vaporization of undecane.[20]

Knudsen-Effusion Method. The vapor pressure for **1BnIMI** was determined by the Knudsen-effusion method, using the technique and procedure described previously.[21] The apparatus consists, essentially, of a stainless steel sublimation chamber immersed in a thermoregulated water jacket and connected to a high-vacuum system ($p = 1 \times 10^{-4}$ Pa). The Knudesn cell was weighed after each experiment in order to determine the mass of sublimed material. The weighings were reproducible to within ± 0.000002 g. The membrane for the effusion measurement of vapor pressure was a tantalum foil, thickness $l = (0.021 \pm 0.004)$ mm. The area of the effusion orifice was, $a = (3.47 \pm 0.02) \times 10^{-3}$ cm^2; the Clausing coefficient[22] $W_a = (0.980 \pm 0.004)$ was found from the expression

$$W_a = 0.0147(l/r)^2 + 0.3490(l/r) + 0.9982 \qquad (1)$$

r being the radius of the effusion orifice. The vapor pressures were calculated using

$$p = (\Delta m/W_a a t)(2\pi RT/M)^{1/2} \qquad (2)$$

where p is the vapor pressure, Δm the mass loss during the time t, W_a the Clausing coefficient of the Knudsen-cell orifice,[22] a the area of the effusion orifice, R the gas constant, T the thermodynamic temperature, and M the molar mass of the studied compound. The molar masses used for the elements were those recommended by the IUPAC in 1995.[23]

Computational Details

The geometries of pyrazole and imidazole as well as those of their *N*-methyl, *N*-ethyl, *N*-phenyl, and *N*-benzyl derivatives were optimized at the B3LYP/6-31G(d) level, which was shown to yield quite reliable geometries for these kinds of systems.[24] The B3LYP approach is a density functional hybrid method which combines the Becke's three parameter nonlocal hybrid exchange potential[25] with the nonlocal correlation functional of Lee, Yang, and Parr.[26]

The harmonic vibrational frequencies were evaluated at the same level of theory in order to confirm that the stationary points found corresponded to local minima of the potential energy surface and to evaluate the zero-point energies (ZPE), which were scaled by the empirical factor 0.98.[27]

To obtain reliable energetics, the final total energies were obtained in single-point calculations at the B3LYP/6-311+G(3df,2p) level, which usually yields thermodynamic properties as proton affinities[28] and enthalpies of formation[29] in fairly good agreement with experimental values. In this respect, it should be mentioned that, recently, Curtiss et al.[29] have shown that the B3LYP density functional method, when used together with a 6-311+G(3df,2p) basis set expansion yields, for a large set of compounds, calculated enthalpies of formation with an average absolute deviation equal to 13.0 kJ mol^{-1}. This set includes the 55 molecules which define the so-called G2 neutral test set and 93 new molecules. A better performance is achieved when using the different G2 approaches, among which the G2 formalism is the most reliable yielding an average absolute deviation of 6.6 kJ mol^{-1}.[29] The performance of the more economic G2(MP2) and G2(MP2,SVP) methods is a little worse, but still quite good with average absolute deviations of 8.1 and 8.5 kJ mol^{-1}, respectively.[29] Unfortunately, although these procedures can be currently used for systems of the size of imidazole and pyrazole, they become prohibitively expensive for derivatives where the substituent is a phenyl or a benzyl group. Hence, for the sake of consistency, we will use for all the derivatives included in this study the B3LYP/611+G(3df,2p)//B3LYP/6-31G(d) approach. To asses the reliability of this approach, these values will be compared with those obtained at the G2(MP2) level for the smaller systems, namely, imidazole and pyrazole and their *N*-methyl and *N*-ethyl derivatives. All these calculations have been carried out using the Gaussian-94 series of programs.[30]

Results and Discussion

Thermodynamic Part. 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

TABLE 1: Typical Combustion Experiments for *N*-Imidazole and *N*-Pyrazole Derivatives at $T = 298.15$ K

	1MeIMI	1MePYR	1BnIMI	1BnPYR
$m(CO_2)$/g	1.45176	1.48565		1.75225
m'(cpd)/g	0.60321	0.62995	0.44368	0.57585
m''(melinex)/g	0.06675	0.05713		0.06359
m''(polyethene)/g			0.05389	
m'''(fuse)/g	0.00343	0.00257		0.00290
ΔT_{ad}/K	1.25902	1.31287	1.2637	1.36967
$\epsilon_{(calor)}/(J\ K^{-1})$	15911.2	15908.3	14253.1	15908.3
$\epsilon_f/(J\ K^{-1})$	16.00	15.88	16.06	15.71
$\Delta m(H_2O)$/g	-0.2	0.0		-0.1
$-\Delta U(IBP)/J^a$	20050.93	20905.28	17981.4	21809.30
$\Delta U(HNO_3)$/J	68.95	67.70	38.8	41.91
ΔU(ign.)/J	0.68	1.10	50.8	0.77
ΔU_Σ/J	12.98	13.44	8.6	13.67
ΔU(melinex)/J	1528.77	1308.32		1456.35
ΔU(polyethene)/J			2498.8	
ΔU(fuse)/J	55.70	41.74		47.10
$-\Delta_c u°/J\ g^{-1}$	30477.83	30913.69	34789.0	35165.88

[a] ΔU(IBP) already includes the ΔU(ign.).

TABLE 2: Individual Values of the Massic Energy of Combustion $\Delta_c u°$ of *N*-Imidazole and *N*-Pyrazole Derivatives at $T = 298.15$ K

1MeIMI	1MePYR	1BnIMI	1BnPYR
	$-\Delta u°/J\ g^{-1}$		
30477.83	30947.30	34790.60	35165.88
30510.95	30913.03	34758.20	35174.13
30478.11	30910.50	34789.00	35158.72
30513.12	30913.69	34790.90	35150.28
30505.60		34759.40	35165.03
30465.06		34795.10	35166.70
30483.43			35178.04
	$-\langle\Delta_c u°\rangle/(J\ g^{-1})^a$		
30490.6 ± 7.2	30921.1 ± 8.7	34780.5 ± 7.0	35165.6 ±3.5

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

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 *N*-Imidazole and *N*-Pyrazole Derivatives at $T = 298.15$ K

	$-\Delta_c U^\circ_m$(cd) kJ mol^{-1}	$-\Delta_c H^\circ_m$(cd) kJ mol^{-1}	$\Delta_f H^\circ_m$(cd) kJ mol^{-1}
1MeIMI	2503.4 ± 3.8	2504.6 ± 3.8	73.1 ± 3.8
1MePYR	2538.8 ± 1.5	2540.0 ± 1.5	108.5 ± 1.6
1BnIMI	5502.4 ± 3.4	5506.1 ± 3.1	141.9 ± 3.4
1BnPYR	5563.3 ± 1.6	5567.0 ± 1.6	202.8 ± 2.1

standard state. The remaining quantities are as previously described.[12]

$$\Delta U(\mathrm{IBP}) = -\{\epsilon(\mathrm{calor}) + \Delta m(\mathrm{H_2O})c_p(\mathrm{H_2O,l}) + \epsilon_f\}\Delta T_{ad} + \epsilon_i(T_i - 298.15) + \epsilon_f(298.15 - T_i - \Delta T_{ad}) + \Delta U_{ign} \quad (3)$$

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 and the standard molar enthalpies of formation for the four 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[31] and in the values of auxiliary quantities.

TABLE 4: Experimental Molar Heat Capacities $C_{p,m}$ of *N*-Imidazole and *N*-Pyrazole Derivatives

T K	$C_{p,m}$ J K^{-1} mol^{-1}	T K	$C_{p,m}$ J K^{-1} mol^{-1}	T K	$C_{p,m}$ J K^{-1} mol^{-1}
		1-methylimidazole			
278.1	176.36	313.4	188.17	348.4	193.62
283.1	178.44	318.4	189.34	353.3	193.89
288.2	180.40	323.4	190.37	358.3	194.04
293.3	182.22	328.4	191.27	363.2	194.07
298.15	183.90	333.4	192.05	368.1	196.81
303.4	185.46	338.4	192.70	370.1	197.15
308.4	186.88	343.4	193.22		
		1-methylpyrazole			
278.1	167.20	312.4	177.59	347.4	188.23
282.1	169.24	317.4	179.24	352.3	190.01
287.2	171.18	322.4	180.28	353.3	193.93
292.3	172.36	327.4	182.85	362.2	197.50
298.15	173.28	332.4	184.46	367.1	201.79
302.4	174.69	337.4	185.09	370.1	203.10
307.4	176.90	342.4	186.26		
		1-benzylimidazole			
278.1	169.51	303.4	184.23	328.4	207.25
283.1	173.25	308.4	188.43	333.4	217.33
288.2	177.35	313.4	190.95	337.4	235.77
293.3	181.73	318.4	195.37		
298.15	182.10	323.5	200.07		
		1-benzylpyrazole			
280.0	254.74	320.0	268.58	365.0	288.42
285.0	255.77	325.0	270.88	370.0	290.09
290.0	257.05	330.0	273.23	375.0	291.55
295.0	258.56	335.0	275.58	380.0	292.78
298.15	259.61	340.0	277.92	385.0	293.74
300.0	260.27	345.0	280.22	390.0	294.42
305.0	262.15	350.0	282.44	392.0	294.61
310.0	264.18	355.0	284.57		
315.0	266.33	360.0	286.57		

TABLE 5: Vapor Pressures of 1-Benzylimidazole

T^a/K	t^b/s	Δm^c/mg	p^d/Pa	$10^2\delta p^e/p$
261.96	25200	2.20	0.595	−0.2
265.24	16560	2.04	0.846	−0.3
269.94	18840	3.78	1.39	0.2
273.78	13560	3.91	2.01	−2
276.51	18480	7.38	2.79	4
281.66	15420	9.41	4.31	−2

[a] Temperature. [b] Time lengh of the experiment. [c] Mass of sublimed substance. [d] Vapor pressure. [e] Fractional deviations of the experimental vapor pressures from the values computed using the eq 4.

To derive $\Delta_f H^\circ_m$(l) from $-\Delta_c H^\circ_m$(l), the standard molar enthalpies of formation of H_2O(l) and CO_2(g), at $T = 298.15$ K, respectively, −(285.830 ± 0.042) kJ mol^{-1} and −(393.51 ± 0.13) kJ mol^{-1}, were used.[32]

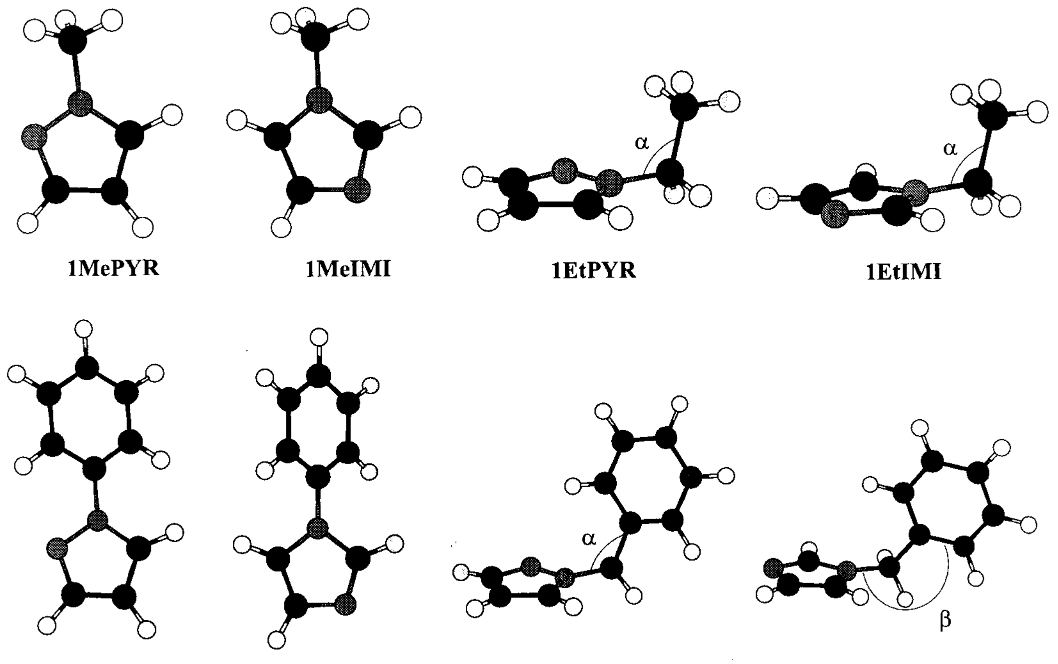
The molar heat capacities for the liquids 1-methylimidazole, 1-methylpyrazole, and 1-benzylpyrazole were measured from $T = 280$ K to the temperature of the vaporization and, for the solid 1-benzylimidazole, from $T = 280$ K to near its melting temperature $T = 338$ K. The temperatures were corrected by a program that includes the calibrations of temperature and power scales of the DSC apparatus, being the obtained values given in Table 4.

The results of our Knudsen-effusion experiments are summarized in Table 5.

An equation of the type

$$\log(p/\mathrm{Pa}) = -B(T/\mathrm{K})^{-1} + A \quad (4)$$

was fitted to the results of Table 5 by the least-squares method. The quantities $\delta p/p$ are the fractional deviations of the experimental vapor pressures from those computed using eq 4. The highest error for the vapor pressure, p, in Table 5 is $5 \times 10^{-3}p$,



1MePYR **1MeIMI** **1EtPYR** **1EtIMI**

1PhPYR **1PhIMI** **1BnPYR** **1BnIMI**

Figure 1. B3LYP/6-31G* optimized geometries of the *N*-substituted azoles showing the relative orientation of the substituents with respect to the azole ring.

TABLE 6: Molar Enthalpies of Vaporization and Sublimation $\Delta_{cd}^{g,T}\Delta H_m^\circ$ at Various Temperatures *T*, for *N*-Imidazole and *N*-Pyrazole Derivatives (p° = 0.1 MPa)

	no. of expts	*T* K	$\Delta_{cd}^{g,T}\Delta H_m^\circ$ kJ mol^{-1}	$\int_{298.15K}^{T} C_{p,m}^\circ(g)dT$ kJ mol^{-1}	$\Delta_{cd}^{g}H_m^\circ$ (298.15 K) kJ mol^{-1}
1MeIMI	5	371	71.9 ± 1.3	7.16	64.7 ± 1.3
1MePYR	6	363	54.4 ± 1.3	6.36	48.0 ± 1.3
1BnIMI	8	298	102.1 ± 0.4		102.1 ± 0.4
1BnPYR	9	386	92.6 ± 2.0	18.79	73.8 ± 2.0

TABLE 7: Derived Standard (p° = 0.1 MPa) Molar Enthalpies of Formation, $\Delta_f H_m^\circ$, of *N*-Imidazole and *N*-Pyrazole Derivatives at *T* = 298.15 K

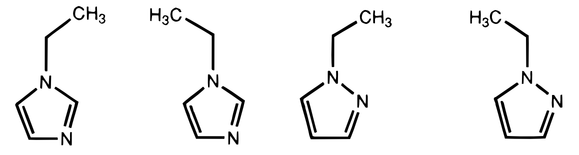
	$\Delta_f H_m^\circ$(cd)/kJ mol^{-1}	$\Delta_{cd}^{g}H_m^\circ$/kJ mol^{-1}	$\Delta_f H_m^\circ$(g)/kJ mol^{-1}
1MeIMI	73.1 ± 3.8	64.7 ± 1.3	137.8 ± 4.0
1MePYR	108.5 ± 1.6	48.0 ± 1.3	156.5 ± 2.1
1BnIMI	141.9 ± 3.4	102.1 ± 0.4	244.1 ± 3.4
1BnPYR	202.8 ± 2.1	73.8 ± 2.0	276.6 ± 2.9

computed as the sum of the estimated errors of all quantities in eq 3. The parameters *A* and *B* for this equation are (16.40 ± 0.06) and −(5332.9 ± 18.7), respectively. The enthalpy of sublimation corresponding to the mean temperature $\langle T\rangle$ = 316.67 K of this experimental range is given in Table 6, and it has been calculated from the corresponding *B* value. The uncertainty assigned to the value of $\Delta_{cr}^{g}H_m$ is based on the standard deviation of the *B* value. The enthalpy of sublimation at *T* = 298.15 K has been computed using the same equation as in ref 33, where $C_{p,m}^\circ$ (cr) has been determined by DSC and $C_{p,m}^\circ$(g) has been calculated using the group contribution scheme of Rihani.[34] The results of measurements of the enthalpies of vaporization and sublimation are given in Table 6. Uncertainties for enthalpies of vaporization are twice the standard deviation of the mean.

The derived enthalpies of formation, in both condensed and gaseous phases, for **1MeIMI**, **1MePYR**, **1BnIMI**, and **1BnPYR** are summarized in Table 7.

Computational Part. Total and relative energies as well as the zero-point vibrational energies of the compounds included in this study are given in Table 8.

SCHEME 1



1EtIMI1 **1EtIMI2** **1EtPYR1** **1EtPYR2**

Geometries. Although a detailed description of the optimized geometries of the *N*-substituted azoles investigated is not the aim of this paper, we have considered it of interest to outline the most significant features.

For the ethyl derivatives, we have initially considered two alternative conformers, namely, **1EtIMI1, 1EtIMI2, 1EtPYR1,** and **1EtPYR2**, which differ in the relative position of the methyl group of the substituent with respect to the azole ring (See Scheme 1). In all cases, both conformers evolve to yield a sole equilibrium conformation, **1EtIMI** and **1EtPYR**, respectively, in which the methyl group is almost perpendicular to the plane of the azole (see Figure 1). Also interestingly, the local structure of the substituent is rather similar for both imidazole and pyrazole, the NCC angle (α in Figure 1) being in both cases around 114°. An almost identical NCC bond angle is predicted for both the *N*-benzyl pyrazole (**1BnPYR**) and the *N*-benzyl imidazole (**1BnIMI**). In these last two cases, the relative orientation of the benzene ring with respect to the azole ring is rather similar for both compounds. Actually, in both cases the CCNC dihedral angle (β in Figure 1) is close to 117°.

Our results also show that the *N*-phenyl derivatives, namely **1PhPYR** and **1PhIMI**, differ in the relative orientation of the phenyl group. Although neither in **1PhPYR** nor in **1PhIMI**, the phenyl group is coplanar with the azole ring, for **1PhPYR** the calculated torsional angle is 20.5°, for the corresponding imidazole is almost twice this value (39.8°), due to a strong repulsive interaction between the hydrogen of the benzene ring and the CH group of the azole. It is worth noting that these torsional angles are in good agreement with the experimental values, 25° for **1PhPYR** and 40° for **1PhIMI**.[35]

TABLE 8: Total Energies (*E*, in hartrees), Zero-Point Energies (ZPE; in hartrees), and Relative Energies (Δ*E*, in kJ mol^{-1}) for *N*-substituted Azoles

	G2(MP2)		B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d)		
compound	*E*	Δ*E*	*E*	ZPE	Δ*E*
imidazole (**1HIMI**)	−225.82659	0.0	−226.29940	0.07126	0.0
pyrazole (**1HPYR**)	−225.80865	46.9	−226.28242	0.07140	44.8
1MeIMI	−265.04689	0.0	−265.62131	0.09913	0.0
1MePYR	−265.03177	39.7	−265.60672	0.09908	38.1
1EtIMI	−304.27450	0.0	−304.95039	0.12784	0.0
1EtPYR	−304.25979	38.5	−304.93602	0.12783	37.7
1PhIMI			−457.41959	0.15224	0.0
1PhPYR			−457.40494	0.15224	38.5
1BnIMI			−496.74408	0.18106	0.0
1BnPYR			−496.72943	0.18115	38.5

TABLE 9: Enthalpies of Formation of *N*-Substituted Azoles[a]

	calcd using atomization energies		calcd using quasiisodesmic reactions 9−13		calcd using quasiisodesmic reactions 14−18		
compound	G2(MP2)	B3LYP[b]	G2(MP2)	B3LYP[b]	G2(MP2)	B3LYP[b]	experimental
imidazole (**1HIMI**)	136.0	123.4	132.2	131.8			132.9 ± 0.6
pyrazole (**1HPYR**)	183.3	168.2	179.1	176.6	163.2	162.3	179.4 ± 0.8
1MeIMI	128.5	125.1	132.6	138.5			137.8 ± 4.0
1MePYR	168.2	176.6	172.4	176.6	145.2	153.1	156.5 ± 2.1
1EtIMI	99.2	108.8	101.7	115.9			110.8 ± 4.3
1EtPYR	138.9	146.4	140.2	153.6	116.3	141.8	132.6 ± 3.3
1PhIMI		287.9		275.7			264.7 ± 4.3
1PhPYR		326.4		314.2		306.7	291.4 ± 4.5
1BnIMI		284.5		269.4			244.1 ± 3.4
1BnPYR		323.0		307.9		293.3	276.6 ± 2.9

[a] All values in kJ mol^{-1} at 298.15 K. [b] Values obtained at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) level of theory.

Calculated Enthalpies of Formation. The enthalpies of formation of the azoles under investigation were initially calculated from the corresponding atomization reactions, following the procedure outlined in ref 29. In this procedure, the enthalpy of formation of a $A_xB_yH_z$ molecule at 0 K in the gaseous state is given by

$$\Delta_f H^\circ_m(A_xB_yH_z,0\ K) = x\Delta_f H^\circ_m(A,0\ K) + y\Delta_f H^\circ_m(B,0\ K) + z\Delta_f H^\circ_m(H,0\ K) - \Sigma D_0 \quad (5)$$

where ΣD_0 is the calculated atomization enthalpy, and $\Delta_f H^\circ_m$(A,0 K), $\Delta_f H^\circ_m$(B,0 K), $\Delta_f H^\circ_m$(H, 0 K) the experimental enthalpies of formation of the isolated atoms at 0 K.

The corresponding enthalpies of formation at 298.15 K in the gaseous state are calculated by correction to $\Delta_f H^\circ_m$(0 K) as follows:

$$\Delta_f H^\circ_m(A_xB_yH_z,298.15\ K) = \Delta_f H^\circ_m(A_xB_yH_z,0\ K) + [H^\circ_m(A_xB_yH_z,298.15\ K) - H^\circ_m(A_xB_yH_z,0\ K)] - x[H^\circ_m(A,298.15\ K) - H^\circ_m(A,0\ K)]_{st} - y[H^\circ_m(B,298.15\ K) - H^\circ_m(B,0\ K)]_{st} - z[H^\circ_m(H,298.15\ K) - H^\circ_m(H,0\ K)]_{st} \quad (6)$$

where the heat capacity correction for the $A_xB_yH_z$ molecule is made using the B3LYP/6-31G(d) harmonic frequencies for the vibrational energy, and adding 3/2*RT* for the translational energy, 3/2*RT* for the rotational energy (*RT* for linear molecules) and the *PV* term. For the elements the heat capacity corrections are for the standard states of the elements and were the same as those listed in ref 29.

The corresponding calculated enthalpies of formation for the imidazoles are given in Table 9. It can be seen that both the G2(MP2) and the B3LYP/6-311+G(3df,2p) estimates, using atomization energies, are in a reasonably good agreement with the experimental values. Actually, if the larger *N*-phenyl and *N*-benzyl derivatives are discarded, the average deviation (11.6 kJ mol^{-1}) is smaller than the average absolute deviation reported in ref 29 for this method. On the other hand it is worth noting that this theoretical approach reproduces well the trends along the series. The enthalpy of formation of the methyl derivative is predicted to be slightly higher than that of the unsubstituted parent compound while the enthalpies of formation of the ethyl and the phenyl derivatives are smaller or sizeably larger, respectively, than that of imidazole, in agreement with the experimental evidence. As expected, the largest deviation, as mentioned above, is found for the *N*-benzyl derivative which is the largest system. This finding is consistent with the conclusions of Petersson et al.[36] in the sense that, when this method is used, the errors tend to be proportional to the size of the molecules.

The deviations found when atomization energies are used can be significantly reduced if appropriate isodesmic reactions are used. In an isodesmic reaction, the number of bonds between each pair of atom types is preserved. Hence, if the error in the calculated bond energy was about the same in both sides of the reaction, the overall error in the calculated reaction enthalpy would be drastically reduced. The next condition to be fulfilled is that the heats of formation of the different molecules which participate in the reaction, but the one whose heat of formation is unknown, should be known as accurately as possible.

For imidazole and pyrazole, these isodesmic reactions would be

$$C_3N_2H_4\ (\mathbf{1HIMI}) + 3CH_4 + 2NH_3 \rightarrow 3CH_3NH_2 + CH_2CH_2 + CH_2NH \quad (7)$$

$$C_3N_2H_4\ (\mathbf{1HPYR}) + 3CH_4 + 2NH_3 \rightarrow CH_3CH_3 + CH_3NH_2 + CH_2CH_2 + CH_2NH + NH_2NH_2 \quad (8)$$

However, these reactions do not fulfill the aforementioned conditions in the sense that the enthalpy of formation of the

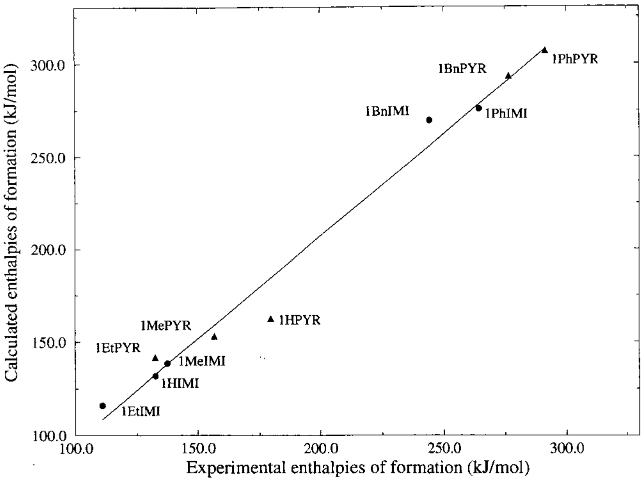


Figure 2. Linear correlation between calculated and experimental enthalpies of formation [$\Delta_f\Delta_f H^\circ_m$(cal.) = (1.10 ± 0.05)$\Delta_f H^\circ_m$(exp.) − (13.5 ± 10.2) kJ mol^{-1}, $R^2 = 0.984$] for the N-substituted imidazoles (●) and N-substituted pyrazoles (▲). For imidazoles, the calculated values were obtained through the use of the quasiisodesmic reactions 9−13, while for pyrazoles, the quasiisodesmic reactions 14−18 were used.

CH_2NH species is not accurately known. In fact, there are, at least, five experimental values for the enthalpy of formation of methylenimine, and these are scattered over ca. 40 kJ mol^{-1} (∼90 ± 20 kJ mol^{-1}).[37] Our theoretically estimated value at the G2 level (86.2 kJ mol^{-1}) is similar to that reported by Pople at the same level (86 kJ mol^{-1})[38] and by Jursic using DFT methods (84 kJ mol^{-1}).[39] In view of this difficulty, we decided to use instead the following reactions:

$$C_3N_2H_4\ (\mathbf{1HIMI}) + CH_4 \rightarrow 2HCN + C_2H_6 \qquad \Delta_r H^\circ_m(298.15\ K) = 128.9\ kJ\ mol^{-1} \quad (9)$$

$$C_4N_2H_6\ (\mathbf{1MeIMI}) \rightarrow 2HCN + C_2H_4 \qquad \Delta_r H^\circ_m(298.15\ K) = 183.3\ kJ\ mol^{-1} \quad (10)$$

$$C_5N_2H_8\ (\mathbf{1EtIMI}) \rightarrow 2HCN + C_3H_6 \qquad \Delta_r H^\circ_m(298.15\ K) = 174.5\ kJ\ mol^{-1} \quad (11)$$

$$C_9N_2H_8\ (\mathbf{1PhIMI}) + CH_4 \rightarrow 2HCN + 3C_2H_2 + C_2H_4 \qquad \Delta_r H^\circ_m(298.15\ K) = 804.6\ kJ\ mol^{-1} \quad (12)$$

$$C_{10}N_2H_{10}\ (\mathbf{1BnIMI}) \rightarrow 2HCN + 4C_2H_2 \qquad \Delta_r H^\circ_m(298.15\ K) = 913.0\ kJ\ mol^{-1} \quad (13)$$

that we shall call from now on quasiisodesmic.

The energies of the different molecules which are involved in these processes were also obtained at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) level, and their experimental enthalpies of formation were taken from Lias et al.[40]

The calculated enthalpies of formation obtained through the use of these quasiisodesmic reactions are now in much better agreement with the experimental values (see Table 9). It can be observed that the largest absolute deviation, excluding the largest derivatives, is only 5 kJ mol^{-1}. Even for the largest derivatives, this absolute deviation (25.3 kJ mol^{-1}) is almost half that obtained when atomization energies are used. The very good agreement between calculated and experimental values is clearly reflected in the goodness of the linear correlation between both sets of values (see Figure 2).

Surprisingly, the agreement is much worse if we use the same isodesmic reactions to estimate the enthalpies of formation of the corresponding *N*-substituted pyrazoles. As illustrated in Table 8, the theoretical scheme used predict the energy gap between *N*-substituted imidazoles and *N*-substituted pyrazoles to be only slightly smaller (ca. 38 kJ mol^{-1}) than that estimated for the unsubstituted parent compounds (44.8 kJ mol^{-1}) and sizeably larger than the gap observed between their experimental enthalpies of formation (ca. 21 kJ mol^{-1}). It is worth noting that this gap is only nicely reproduced for the couple imidazole/pyrazole but is clearly overestimated for the *N*-substituted derivatives. A possible origin for this disagreement is the inadequacy of the isodesmic reactions 9−13 for the particular case of pyrazoles, which present a N−N linkage, which does not exist in the case of imidazoles. Very likely, HCN is not a good reference compound in this particular cases and should be replaced by hydrazine ($H_2N{-}NH_2$).

It is not easy in this case to accommodate the total number of atoms when one of the reference systems is hydrazine. Hence, the only quasiisodesmic reactions we found reasonable are

$$C_3N_2H_4\ (\mathbf{1HPYR}) + CH_4 \rightarrow N_2H_4 + 2C_2H_2 \qquad \Delta_r H^\circ_m(298.15\ K) = 464.0\ kJ\ mol^{-1} \quad (14)$$

$$C_4N_2H_6\ (\mathbf{1MePYR}) + C_2H_4 \rightarrow N_2H_4 + 3C_2H_2 \qquad \Delta_r H^\circ_m(298.15\ K) = 574.0\ kJ\ mol^{-1} \quad (15)$$

$$C_5N_2H_8\ (\mathbf{1EtPYR}) + C_3H_6 \rightarrow N_2H_4 + 3C_2H_2 + C_2H_4 \qquad \Delta_r H^\circ_m(298.15\ K) = 669.4\ kJ\ mol^{-1} \quad (16)$$

$$C_9N_2H_8\ (\mathbf{1PhPYR}) + C_3H_8 \rightarrow N_2H_4 + 6C_2H_2 \qquad \Delta_r H^\circ_m(298.15\ K) = 1261.5\ kJ\ mol^{-1} \quad (17)$$

$$C_{10}N_2H_{10}\ (\mathbf{1BnPYR}) + C_2H_6 \rightarrow N_2H_4 + 6C_2H_2 \qquad \Delta_r H^\circ_m(298.15\ K) = 1254.4\ kJ\ mol^{-1} \quad (18)$$

The enthalpies of formation obtained are now in much better agreement with the experimental values, with only the exception of the unsubstituted parent compound. Unfortunately, these results are not conclusive, since although the agreement with the experimental values is better, this seems to be a consequence of the fact that all the heats of formation, including that of the parent compound, are smaller, while what the experimental results actually indicate is that the substituent effects are not quantitatively equal in imidazoles and pyrazoles. For instance, if we consider the *N*-methyl derivatives, the experimental values show that while the methyl substitution effect is negligibly small for the imidazole, it is sizeably large for the pyrazole, and this fact is not reproduced by the theoretical calculations, independently of the quasiisodesmic reactions used. In this respect, it is important to mention that both situations are found for other systems. For instance, while the methyl substitution effect on the heat of formation of benzene is quite large [$\Delta_f H^\circ_m$ (benzene) = 82.4 kJ mol^{-1}, $\Delta_f H^\circ_m$ (toluene) = 50.2 kJ mol^{-1}],[40] the same effect on the heat of formation of hydrazine is negligibly small [$\Delta_f H^\circ_m$ (NH_2NH_2) = 95.4 kJ mol^{-1}, $\Delta_f H^\circ_m$ (CH_3NHNH_2) = 95.4 kJ mol^{-1}].[40]

The first question we need to answer is whether our theoretical scheme is able to reproduce this different behavior. For the particular case of benzene and toluene, we have chosen the following isodesmic reactions:

$$C_6H_6 \rightarrow 3C_2H_2 \qquad \Delta_r H^\circ_m(298.15\ K) = 605.0\ kJ\ mol^{-1} \quad (19)$$

$$C_7H_8 + CH_4 \rightarrow 3C_2H_2 + C_2H_6$$

$$\Delta_r H_m^\circ(298.15\ \mathrm{K}) = 615.5\ \mathrm{kJ\ mol^{-1}} \quad (20)$$

From the enthalpies of these reactions, we could estimate the enthalpies of formation of benzene and toluene to be 79.1 kJ mol^{-1} and 59.0 kJ mol^{-1}, which are in fairly good agreement with the experimental values (82.4 and 50.2 kJ mol^{-1}, see previously).[40]

For the particular case of hydrazine and methylhydrazine we have used, as before, the procedure based on their atomization energies. The results obtained, 84.1 kJ mol^{-1} and 88.3 kJ mol^{-1}, respectively are also in nice agreement with the experimental values, and clearly predict a rather small substituent effect.

In summary, the experimental enthalpies of formation of the *N*-substituted imidazoles are very well reproduced by our calculations, but the agreement for the particular case of pyrazoles is worse. This is so because while the theory predicts that substituent effects on the enthalpies of formation are rather similar for imidazoles and pyrazoles, the experimental values show that this effect is larger for pyrazoles than for imidazoles. Unfortunately from our study the origin of this small discrepancy is not clear.

Conclusions

Accurate experimental enthalpies of formation measured using static bomb combustion calorimeter, “vacuum sublimation” drop calorimeter method, and Knudsen-effusion method have been reported for **1MeIMI**, **1MePYR**, **1BnIMI**, and **1BnPYR**. For the series of *N*-substituted imidazoles, these values, together with those reported in the literature, are in very good agreement with the corresponding theoretical estimates obtained using the B3LYP/6-311*G(3df,2p)//6-31G(d) approach, when the appropriate quasiisodesmic reactions are used. The agreement is slightly worse when the corresponding atomization energies are used. The agreement between experimental and calculated values is worse for the series of the *N*-substituted pyrazoles, in particular as far as the differences with respect to the analogous imidazoles are concerned. Experimentally, the gap between the enthalpies of formation of imidazoles and pyrazoles decreases significantly upon *N*-substitution, while the theoretical estimates indicate that this decrease is significantly smaller. The origin of this small discrepancy is not at all clear.

The example here reported, **R^1-IMI** vs **R^1-PYR**, is a particular case of the more general problem of substituent effects. Concerning the problem addressed in the Introduction, i.e., the comparison of effects through the nitrogen (diazoles) vs effects through the carbon (benzenes),[40] the results for five substituents (H, Me, Et, Ph, and Bn) show that these effects are approximately the same (slopes of the regression lines between 1.01 and 1.13).

$$\mathbf{R^1\text{-}PYR} = (28 \pm 17) + (1.01 \pm 0.09)\mathbf{R^1\text{-}IMI}, \quad n = 5,\ R^2 = 0.977 \quad (21)$$

$$\mathbf{R^1\text{-}PYR} = (98 \pm 14) + (1.13 \pm 0.12)\mathbf{R^1\text{-}BEN}, \quad n = 5,\ R^2 = 0.964 \quad (22)$$

$$\mathbf{R^1\text{-}IMI} = (73 \pm 20) + (1.09 \pm 0.18)\mathbf{R^1\text{-}BEN}, \quad n = 5,\ R^2 = 0.928 \quad (23)$$

TABLE 10: Application of the Hess’s Law[a]

R^1 substituents	quasiisodesmic reactions 9−13 **PYR−IMI**	experimental **PYR−IMI**	experimental **PYR−BEN**[b]	experimental **IMI−BEN**[b]
H	44.8	46.5 ± 1.4	96.8	50.3
Me	38.1	18.7 ± 6.1	106.1	87.4
Et	37.7	21.8 ± 7.6	102.7	80.9
Ph	38.5	26.7 ± 8.8	110.0	83.3
Bn	38.5	32.5 ± 6.3	137.6	105.0
average	39.5	29.2	110.6	81.4

[a] All values in kJ mol^{-1} at 298.15 K. [b] Benzene, toluene, ethylbenzene, biphenyl, and diphenylmethane data from ref 20.

This is a simple consequence of the Hess’s law which states that the differences (24−26) must be constant, i.e., that the slopes should be 1:

$$[\mathbf{R^1\text{-}IMI}] - [\mathbf{R^1\text{-}PYR}] = \mathrm{const_{IP}} \approx 29 \qquad (24)$$

$$[\mathbf{R^1\text{-}PYR}] - [\mathbf{R^1\text{-}BEN}] = \mathrm{const_{PB}} \approx 111 \qquad (25)$$

$$[\mathbf{R^1\text{-}IMI}] - [\mathbf{R^1\text{-}BEN}] = \mathrm{const_{IB}} \approx 81 \qquad (26)$$

The value of these constants depends on the isodesmic or quasiisodesmic reactions selected, **but not on R^1**. However, an examination of these differences (Table 10) shows large fluctuations, even for calculated values (although in this case it affects only the **1H** derivatives). We have no explanation for these anomalies which seem to affect mainly the **1H** and **1Bn** substituents.

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