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Substituent Effects on Enthalpies of Formation of Nitrogen Heterocycles: 2-Substituted Benzimidazoles and Related Compounds

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The enthalpies of combustion, heat capacities, enthalpies of sublimation and enthalpies of formation of 2-*tert*-butylbenzimidazole (**2*t*BuBIM**) and 2-phenylimidazole (**2PhIM**) are reported and the results compared with those of benzene derivatives and a series of azoles (imidazoles, pyrazoles, benzimidazoles and indazoles). Theoretical estimates of the enthalpies of formation were obtained through the use of atom equivalent schemes. The necessary energies were obtained in single-point calculations at the B3LYP/6-311++G(d,p) on B3LYP/6-31G* optimized geometries. The comparison of experimental and calculated values of all studied compounds bearing H (unsubstituted), methyl (**Me**) ethyl (**Et**), propyl (**Pr**), isopropyl (***i*Pr**), *tert*-butyl (***t*Bu**), benzyl (**Bn**) and phenyl (**Ph**) groups show remarkable homogeneity. The remarkable consistency of both the calculated and experimental results allows us to predict with reasonable certainty the missing experimental values. The crystal and molecular structure of the 2-benzylbenzimidazole (**2BnBIM**) has been determined by X-ray analysis. The observed molecular conformation permits the crystal being built up through N−H···N hydrogen bonds and van der Waals contacts between the molecules. An attempt has been made to relate the crystal structure to the enthalpies of sublimation.

Introduction

Enthalpies of formation are crucial thermodynamic quantities. They are needed to estimate the amount of energy released or absorbed in a chemical reaction, to calculate other thermodynamic functions and, what is more important, to asses the stability of a molecule. Unfortunately, this is not always experimentally available because of the difficulties inherent to the usual experimental procedures, and sometimes, due to the difficulty in having a pure sample of the compound whose enthalpy of formation is going to be measured. In other cases, the systems of interest are of low stability or even elusive to experimental observation. This situation can be partially alleviated by means of computational chemistry techniques. Quantitative determination of thermodynamic properties of a molecule by using standard quantum chemical procedures is a long-sought goal of computational chemistry.

In a series of previous papers we have reported the enthalpies of formation of a set of 2-substituted benzimidazoles (see Chart 1) (that of benzimidazole **BIM** itself was already known),[1] **2MeBIM**,[2] **2EtBIM**,[2] **2PrBIM**,[3] **2*i*PrBIM**,[3] **2BnBIM**[4] and **2PhBIM**.[4] That of **2*t*BuBIM** will be described in the present paper. A similar study of benzene derivatives bearing the same substituents **Bz**, **2MeBz**, **2EtBz**, **2PrBz**, **2*i*PrBz**, **2*t*BuBz**, **2BnBz** and **2PhBz** was also carried out.[5]

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CHART 1: Structures of the Eight Benzimidazoles

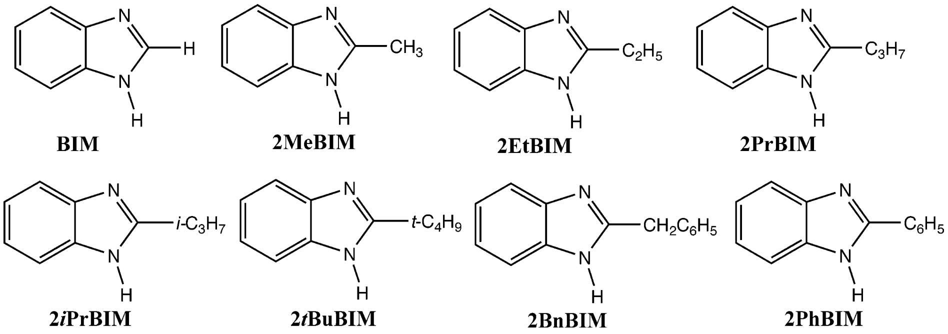
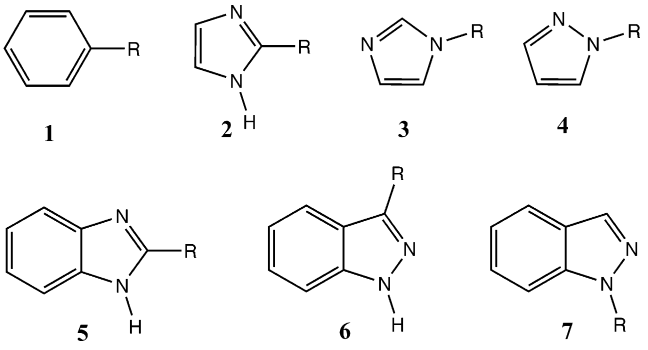


CHART 2: Structures of Benzene 1 and the Six Heterocyclic Compounds 2−7



The main aim of this paper is to carry out a comparative study of the experimental and calculated thermodynamic properties of five families of compounds (Chart 2), benzenes **1**,[5] 2-substituted imidazoles **2**,[1,6] *N*-substituted imidazoles **3**,[5,7] *N*-substituted pyrazoles **4**,[5,8] and 2-substituted benzimidazoles **5**,[1] to assess the transferability of substituent effects or their dependence on the nature of the ring to which they are attached. If reasonably good correlations exist between the enthalpies of formation of the different families, they could be used to predict the unknown enthalpies of formation of closely related compounds. For this purpose we have considered the families of 3-substituted **6** and 1-substituted indazoles **7** (see Chart 2).

For the comparison of the five series of azoles **1**−**5** and because only three values of 2-substituted imidazoles **2** were known (H **IM**, CH_3 **2MeIM**, C_2H_5 **2EtIM**), it was decided to measure the enthalpy of formation of a fourth compound, **2**, R = Ph, **2PhIM**.

We attempt also to analyze possible relationships between crystal structures and enthalpies of formation. For this purpose we have considered as suitable model systems benzimidazole and its 2-benzyl derivative. The X-ray molecular structure of **BIM** was known,[9,10] and that of **2BnBIM** will be described here.

The organization of this final paper will be (i) an experimental section concerning the calorimetry measurements and crystallography determinations, (ii) the determination of $\Delta_f H°$(exp) for **2*t*BuBIM**, the only missing compound in the series of 2-substituted benzimidazoles derivatives, and the X-ray molecular structure of **2BnBIM**, (iii) comparative discussion of the enthalpies of formation of benzenes **1**, 2-substituted imidazoles **2**, *N*-substituted imidazoles **3** and pyrazoles **4** and 2-substituted benzimidazoles **5** with the same eight substituents (Chart 2), and (iv) analysis of the possible link between crystal structures and enthalpies of formation of benzimidazoles.

Experimental Section

All the compounds have been described in previous papers,[2−4] except 2-*tert*-butylbenzimidazole **2*t*BuBIM** and 2-phenylimidazole **2PhIM**. **2*t*BuBIM** [CAS 24425-13-6] is a commercial compound (Lancaster). The commercial sample was supplied with 98% purity and was purified by repeated discolorations over activated carbon and crystallizations (in dichloromethane/hexane 2:1) until the purity determined by differential scanning calorimetry (DSC) [Seiko 220C calorimeter] reached 0.9994 mass fraction. The melting point determined by DSC is 593.5 K. **2-PhIM** [CAS 670-96-2] is a commercial compound (Aldrich). The commercial sample was supplied with 98% purity and was purified by repeated discolorations over activated carbon and crystallization (in dichloromethane/hexane 2:1), until the purity determined by DSC [Seiko 220C calorimeter] reached 0.9994 mass fraction. The melting point determined by DSC is 421.4 K.

Combustion Calorimetry of 2-*tert*-Butylbenzimidazole (2*t*BuBIM) and of 2-Phenylimidazole (2PhIM). The combustion experiments were performed with an isoperibol calorimetric system, with a static bomb (Parr instrument, model 1108); apparatus and procedure have been described elsewhere.[11,12] Combustion of certificated benzoic acid BCS-CRM 190r was used for calibration of the bomb. Its specific energy of combustion is $-26\,432.3 \pm 3.8$ J 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 six calibration experiments, $\epsilon(\text{calor}) = 16\,007.3 \pm 0.7$ J K^{-1}, where the uncertainty quoted is the standard deviation of the mean. For the combustion experiments of 2-phenylimidazole the same calorimetric system was used after some small changes on the metal mechanical parts were carried out, so another calibration of the system was performed, in the same experimental conditions, with certificated benzoic acid NIST standard reference sample 39j, having a specific energy of combustion of $-26\,434 \pm 3$ J g^{-1}, under certificate conditions. From eight calibration experiments, $\epsilon(\text{calor}) = 15\,905.7 \pm 1.0$ 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. Two different samples of hexadecane (Aldrich Gold Label, mass fraction >0.99) were used as an auxiliary of the combustion measurements and their standard massic energy of combustion were measured separately to be $-\Delta_c u°(\text{l})/(\text{J g}^{-1}) = 47\,158.4 \pm 3.3$ for the sample used on the combustions of 2-*tert*-butylbenzimidazole, and $-\Delta_c u°(\text{l})/(\text{J g}^{-1}) = 47\,160.8 \pm 4.1$, for the sample used in the combustions of 2-phenylimidazole, both in agreement with the value of Fraser and Prosen[13] for a sample of purity mass fraction 0.9996, $-\Delta_c u°(\text{l})/(\text{J g}^{-1}) = 47\,155.0 \pm 3.8$. Samples in pellet form were ignited at $T = 298.150 \pm 0.001$ K in oxygen, at pressure $p = 3.04$ MPa, with a volume of 1 cm^3 of water added to the bomb. 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 of empirical formula $CH_{1.686}O_{0.843}$, $-\Delta_c u^o = 16\,250$ J g^{-1},[14] a value that has been confirmed in the Porto Laboratory. The corrections for nitric acid formation were based on -59.7 kJ mol^{-1},[15] for the molar energy of formation of 0.1 mol dm^{-3} $HNO_3(aq)$ from N_2, O_2, and $H_2O(l)$. Corrections for carbon residue soot formation were based[16] on $\Delta_c u^o = -33$ kJ g^{-1}.

The amounts of 2-*tert*-butylbenzimidazole and of 2-phenylimidazole used in each experiment were determined from the total mass of carbon dioxide produced after allowance for that formed from the cotton thread fuse and hexadecane. All the necessary weighing was made in a Mettler Toledo AT201 microbalance, sensitivity $\pm 1 \times 10^{-6}$ g, and corrections from apparent mass to mass were made. The average ratio of mass of carbon dioxide recovered after combustions to that calculated from the mass of the samples was 0.999 99 ± 0.000 02 in the case of 2-*tert*-butylbenzimidazole and 0.999 99 ± 0.000 02 in the case of 2-phenylimidazole, where the uncertainties are the standard deviations of the mean. The density, at $T = 298.15$ K, for 2-*tert*-butylbenzimidazole is 1.008 g cm^{-3}. An estimated pressure coefficient of specific energy: $(\partial u/\partial p)_T = -0.2$ J g^{-1} MPa^{-1} at $T = 298.15$ K, a typical value for most organic solid compounds,[17] was assumed. For each compound, the massic energy of combustion, $\Delta_c u^o$, was calculated by the procedure given by Hubbard et al.[16]

The molar masses used for the elements were those recommended by the IUPAC in 2001,[18] yielding the molar mass of 174.234 g mol^{-1} for 2-*tert*-butylbenzimidazole and 146.1891 g mol^{-1} for 2-phenylimidazole.

High-Temperature Calvet Microcalorimetry. The enthalpy of sublimation of 2-*tert*-butylbenzimidazole was measured using the "vacuum sublimation" drop microcalorimetric method.[19,20] Samples, about 3−5 mg of the 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 (SETARAM HT 1000 D), held at $T = 558$ K, and then removed from the hot zone by vacuum sublimation.

The observed enthalpies of sublimation were corrected to $T = 298.15$ K, using the value of $\Delta_{298.15K}^{558K} H_m^o(g)$ estimated by the Benson's Group Method,[21] using values from Stull et al.[22] The microcalorimeter was calibrated in situ for these measurements using the reported enthalpy of sublimation of naphthalene: $\Delta_{cr}^{g} H_m^o(C_{10}H_8) = 72.51 \pm 0.01$ kJ mol^{-1}.[23]

Vapor Pressure Measurements. The vapor pressures of the crystals of 2-phenylimidazole were measured, at several temperatures, by the mass-loss Knudsen-effusion technique on an apparatus enabling the simultaneous operation of nine aluminum effusion cells. This apparatus has been tested by measuring vapor pressures between 0.1 and 1 Pa, over temperature ranges of ca. 20 K, of benzoic acid, phenanthrene, anthracene, benzanthrone and 1,3,5-triphenylbenzene.[24] Both the measured vapor pressures and the derived enthalpies of sublimation of the test substances are in excellent agreement with the literature results for those compounds. The nine effusion cells are contained in cylindrical holes inside three aluminum blocks, three cells per block. Each block is kept at a constant temperature, different from the other two blocks.[24]

The measurements were extended through a chosen temperature interval corresponding to measured vapor pressures in the range 0.1−1.0 Pa. In a typical effusion experiment the loss of mass Δm of the samples, during a convenient effusion time period t, is determined by weighing the effusion cells to ±0.01 mg before and after the effusion period in a system evacuated to a pressure near 1×10^{-4} Pa. The samples are assumed to be in thermal equilibrium, to ±0.001 K, with the aluminum blocks. At the temperature T of the experiment, the vapor pressure p is calculated by

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

where M is the molar mass of the effusing vapor, R is the gas constant, A_o is the area of the effusion hole and w_o is the respective Clausing factor[25] calculated by eq 2, where l is the thickness of the effusion hole and r its radius:

$$w_o = \{1 + (3l/8r)\}^{-1} \qquad (2)$$

The areas and Clausing factors of the used effusion orifices in platinum foil of 0.0125 mm thickness are presented in the electronic supplementary information (Table S1)

Heat Capacity Measurements. A differential scanning calorimeter (Perkin-Elmer, Pyris 1) equipped with an intracooler unit was used in this research to determine the heat capacities of the compounds. Its temperature scale was calibrated by measuring the melting temperature of the recommended high-purity reference materials: benzoic acid,[26] tin,[27] and indium.[27] The power scale was calibrated with high-purity indium (mass fraction: >0.99999) as reference material.[28] Thermograms of samples hermetically sealed in aluminum pans were recorded in a nitrogen atmosphere. All the pans were weighed before and after the experiments to confirm that no product had volatilized. The samples were weighed on a Mettler AT21 microbalance with a sensitivity of 1×10^{-6} g. Heat capacities were determined by the "scanning method" following the methodology described in the literature[29−32] and using synthetic sapphire (α-aluminum oxide) as reference material.[28] For heat capacity determinations, four to six samples weighing 10−25 mg were scanned in the temperature range from $T = 268$ to 454 K, using a heating rate of 0.17 K s^{-1}. To check the experimental method, heat capacity experiments with synthetic sapphire (α-aluminum oxide) and benzoic acid as reference materials,[28,29] in the temperature intervals $T = 268-360$ K and $T = 268-410$ K, respectively, were made. The measurements for heat capacity determination had an accuracy between 0.3 and 1.6% and details are given in ref 29.

X-ray Crystallographic Analysis of 2BnBIM. Crystallization solvent: dichloromethane/hexane. A summary of data collection and refinement process is given in Table S2 of the Supporting Information. All non-hydrogen atoms were found by direct methods, SIR92,[33] and all hydrogen atoms were located on the corresponding difference Fourier syntheses. The structure was refined with a full matrix least squares procedure on Fobs using 545 observed reflections with $I > 2\sigma(I)$. Owing to the low value of the ratio of freedom (3), we refined alternatively positions, thermal parameters and hydrogen coordinates so as to use rations of freedom of about 5. The atomic scattering factors were taken from the International Tables for X-ray Crystallography[34] and most of the calculations were carried out with the XTAL,[35] PESOS[36] and PARST[37] programs running on an AXP 600 computer.

Theoretical Section. Many different theoretical schemes have been proposed in the literature to estimate enthalpies of formation. Among the most accurate and simpler ones are those based in atom equivalent or group equivalent components.[38−44] In this paper we shall use one of these approaches proposed by

TABLE 1: Results for a Typical Combustion Experiment of Each Compound,[a] at $T = 298.15$ K

	2-*tert*-butylbenzimidazole	2-phenylimidazole
m(CO$_2$, total)/g	1.465 18	1.784 37
m'(cpd)/g	0.404 65	0.423 30
m''(fuse)/g	0.004 24	0.002 43
m'''(hexadecane)/g	0.107 43	0.199 02
ΔT_{ad}/K	1.229 43	1.478 54
ϵ_f/J K^{-1}	16.12	16.31
Δm(H$_2$O)/g	0.1	0.0
$-\Delta U$(IBP)^b/J	19 699.19	23 540.40
ΔU(fuse)/J	68.86	39.46
ΔU(hexadecane)/J	5066.37	9385.78
ΔU(HNO$_3$)/J	35.52	40.54
ΔU(ign)/J	1.00	0.93
$-\Delta U$(carbon)/J		4.95
ΔU_Σ/J	9.07	11.90
$-\Delta_c u°$/J g^{-1}	35 881.30	33 233.33

[a] m(CO$_2$, total) is the mass of CO$_2$ recovered in each combustion; m(cpd) is the mass of compound burnt in each experiment; m(fuse) is the mass of fuse (cotton) used in each experiment; m(hexadecane) is the mass of hexadecane used as auxiliary of combustion in each experiment; ΔT_{ad} is the corrected temperature rise; ϵ_f is the energy equivalent of contents in the final state; Δm(H$_2$O) is the deviation of mass of water added to the calorimeter from 3119.6 g; ΔU(IBP) is the energy change for the isothermal combustion reaction under actual bomb conditions; ΔU(fuse) is the energy of combustion of the fuse (cotton); ΔU(hexadecane) is the energy of combustion of hexadecane used as the auxiliary of combustion; ΔU(HNO$_3$) is the energy correction for the nitric acid formation; ΔU(ign) is the electrical energy for ignition; ΔU(carbon) is the energetic correction for the formation of carbon residue soot; ΔU_Σ is the standard state correction; $\Delta_c u°$ is the standard massic energy of combustion. [b] ΔU(IBP) already includes the ΔU(ign).

Cioslowski et al.[43] because it has been shown to perform well when dealing with other nitrogen heterocycles and with different benzene derivatives.[5] The geometries of the 2-substituted benzimidazoles were optimized at the B3LYP/6-31G* level. Harmonic vibrational frequencies were calculated also at this level, to assess that the stationary points found corresponded to local minima of the potential energy surface and to estimate the corresponding zero point energies (ZPE). To apply the atom equivalent scheme of Cioslowski et al.,[43] B3LYP/6-311++G(d,p) geometries and energies were also evaluated using as starting structures the B3LYP/6-31G* ones. The B3LYP functional, as implemented in the Gaussian-98 suite of programs,[45] combines Becke three-parameter nonlocal hybrid exchange potential[46] and the nonlocal correlation functional of Lee, Yang, and Parr.[47]

Results and Discussion

Detailed results for a typical combustion experiment of each compound are given in Table 1: Δm (H$_2$O) is the deviation of the mass of water added to the calorimeter from 3119.6 g, the mass assigned for ϵ(calor), ΔU_Σ is the correction to the standard state and the remaining terms are as previously described.[16] The detailed results for all the combustion experiments of each compound, together with the mean value of the massic energies of combustion, $\Delta_c u^o$, are presented in the Supporting Information (Table S3 for 2-*tert*-butylbenzimidazole and Table S4 for 2-phenylimidazole). Table 2 presents the individual values of the massic energy of combustion, $\Delta_c u^o$ and the standard deviation of the mean, for 2-*tert*-butylbenzimidazole and 2-phenylimidazole, at $T = 298.15$ K

TABLE 2: Individual Values of the Massic Energy of Combustion, $\Delta_c u°$ (J g^{-1}), of 2-*tert*-Butylbenzimidazole and 2-Phenylimidazole, at $T = 298.15$ K

$-\langle\Delta_c u°\rangle$	
2-*tert*-butylbenzimidazole	2-phenylimidazole
35 874.47	33 233.33
35 881.30	33 242.95
35 880.54	33 242.02
35 876.37	33 238.96
35 871.91	33 235.34
35 876.98	33 230.49
35 876.9 ± 1.5[a]	33 237.2 ± 2.0[a]

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

TABLE 3: Derived Standard ($p° = 0.1$ 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, $\Delta_f H^o_m$, for the Compounds at $T = 298.15$ K (kJ mol^{-1})

compound	$-\Delta_c U^o_m$(cr)	$-\Delta_c H^o_m$(cr)	$\Delta_f H^o_m$(cr)
2-*tert*-butylbenzimidazole	6251.4 ± 1.5	6257.6 ± 1.5	71.8 ± 2.1
2-phenylimidazole	4792.0 ± 1.3	4794.5 ± 1.3	109.6 ± 1.8

For the static bomb measurements, as samples were ignited at $T = 298.150 \pm 0.001$ K,

$$\Delta U(\text{IBP}) = -\{\epsilon(\text{calor}) + c_p(\text{H}_2\text{O,l})\, \Delta m(\text{H}_2\text{O}) + \epsilon_f\}\Delta T_{ad} + \Delta U(\text{ign}) \quad (3)$$

These values of $\Delta_c u^o$ are referred to the combustion reactions according to

$$\text{C}_n\text{H}_m\text{N}_2(\text{cr}) + \frac{4n + m}{2}\text{O}_2(\text{g}) \rightarrow n\text{CO}_2(\text{g}) + \frac{m}{2}\text{H}_2\text{O}(\text{l}) + \text{N}_2(\text{g}) \quad (4)$$

Table 3 lists the derived standard molar energies and enthalpies of combustion and the standard molar enthalpies of formation for the compounds, in the crystalline state, at $T = 298.15$ K. In accordance with normal thermochemical practice, the uncertainties assigned to the molar enthalpies of combustion and formation are twice the overall standard deviations of the mean and include the uncertainties in calibration and in the auxiliary quantities used.[48,49] To derive $\Delta_f H^o_m$(cr) from $\Delta_c H^o_m$(cr), the standard molar enthalpies of formation for H$_2$O(l), -285.830 ± 0.042 kJ mol^{-1},[50] and for CO$_2$(g), -393.51 ± 0.13 kJ mol^{-1},[50] were used.

Detailed results of the measurements of the enthalpy of sublimation of 2-*tert*-butylbenzimidazole are given in the Supporting Information (Table S5). From seven independent determinations at $T = 558$ K, the average value of the observed enthalpies of sublimation, $\Delta^{\text{g},558\text{K}}_{\text{cr},298.15\text{K}} H_m = (187.49 \pm 2.92)$ kJ mol^{-1}, where the uncertainty assigned is twice the standard deviation of the mean. The enthalpic correction to the reference temperature $T = 298.15$ K, estimated by the Benson's Group method[21] using values from Stull et al.[22] is $\Delta^{558\text{K}}_{298.15\text{K}} H^o_m = 72.38$ kJ mol^{-1}, thus yielding the value of the standard molar enthalpy of sublimation $\Delta^g_{cr} H^o_m(298.15\text{ K}) = 115.1 \pm 2.9$ kJ mol^{-1}.

The integrated form of the Clausius−Clapeyron equation, $\ln(p/\text{Pa}) = a - b(T/\text{K})^{-1}$, where a is a constant and $b = \Delta^g_{cr} H^o_m(\langle T\rangle)/R$, was used to derive the standard molar enthalpy of sublimation at the mean temperature of the experimental temperature range for 2-phenylimidazole. The experimental results obtained from each effusion cell, together with the

TABLE 4: Experimental Results for 2-Phenylimidazole, Where a and b Are from the Clausius−Clapeyron Equation $\ln(p/\mathrm{Pa}) = a - b\,(\mathrm{k}/T)$, and $b = \Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(\langle T\rangle)/R$; $R = 8.314\,51$ J K^{-1} mol^{-1}

hole number	a	b	$\langle T\rangle$/K	$p(\langle T\rangle)$/Pa	$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(\langle T\rangle)$/kJ mol^{-1}
A1−A2−A3	35.70 ± 0.33	13 214 ± 118			109.9 ± 0.5
B4−B5−B6	36.39 ± 0.20	13 480 ± 72			112.1 ± 0.3
C7−C8−C9	35.89 ± 0.17	13 306 ± 61			110.6 ± 0.2
global results	35.81 ± 0.42	13 267 ± 152	364.215	0.540	110.3 ± 0.6

TABLE 5: Derived Standard ($p^\circ = 0.1$ MPa) Molar Enthalpies of Formation, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}$, and of Sublimation, $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$, at $T = 298.15$ K (kJ mol^{-1})

	$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}$(cr)	$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$	$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}$(g)
2-*tert*-butylbenzimidazole	−71.8 ± 2.1	115.1 ± 2.9	43.3 ± 3.3
2-phenylimidazole	109.6 ± 1.8	113.6 ± 0.6	223.2 ± 1.9

residuals of the Clausius−Clapeyron equation, derived from least squares adjustment are presented in Table S6 of the Supporting Information.

Table 4 presents for each set of holes used and for the global treatment of all the (p, T) points obtained for 2-phenylimidazole, the detailed parameters of the Clausius−Clapeyron equation together with the calculated standard deviations and the standard molar enthalpies of sublimation at the mean temperature of the experiments $T = \langle T\rangle$, and the equilibrium pressure at this temperature $p(T = \langle T\rangle)$. The calculated enthalpies of sublimation obtained from each set of individual holes are in reasonable agreement within experimental error. The sublimation enthalpy, at the temperature 298.15 K, was derived from the sublimation enthalpy calculated at the mean temperature $\langle T\rangle$ of the experiments, by

$$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(T{=}298.15\ \mathrm{K}) = \Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(\langle T\rangle) + \Delta_{\mathrm{cr}}^{\mathrm{g}}c_{p,\mathrm{m}}^{\mathrm{o}}(298.15\ \mathrm{K} - \langle T\rangle) \quad (5)$$

The value of $\Delta_{\mathrm{cr}}^{\mathrm{g}}c_{p,\mathrm{m}}^{\mathrm{o}}$ was estimated as $\Delta_{\mathrm{cr}}^{\mathrm{g}}c_{p,\mathrm{m}}^{\mathrm{o}} = -50$ J K^{-1} mol^{-1}, in accordance with similar estimations made by other authors[51] that we have already used in previous papers for other organic compounds.[52−56] So, the standard molar enthalpy of sublimation of 2-phenylimidazole, at $T = 298.15$ K, has been derived as $\Delta_{\mathrm{cr}}^{\mathrm{g}}c_{p,\mathrm{m}}^{\mathrm{o}}(\mathrm{2PhIM}) = 113.6 \pm 0.6$ kJ mol^{-1}.

From the values, at $T = 298.15$ K, of $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}$(cr) and of $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$, the derived standard molar enthalpies of formation, in gaseous phase, for 2-*tert*-butylbenzimidazole **2*t*BuBIM** and for 2-phenylimidazole **2PhIM** were calculated and registered in Table 5.

Results of Heat Capacity Measurements. The molar heat capacities for **2*t*BuBIM** were measured from $T = 268$ to 454 K. The experimental values were fitted to a second-order polynomial given as eq 6. No phase transitions were found in this temperature interval. Detailed values of measured C_{pm} at fixed temperatures are given in Table S7.

$$\mathrm{C}_{pm} = -2.397 \times 10^{5}(T/\mathrm{K})^2 + 0.7126(T/\mathrm{K}) + 9.04041 \qquad r^2 = 0.9995 \quad (6)$$

X-ray Structure Determination. The molecular structure and the atom labeling are depicted in Figure 1. Table 6 shows a summary of the geometrical parameters of the molecule. The twist around the C2−C10 and C10−C11 bonds bring about angles of 73.6(5)° between the benzimidazole and phenyl plane.

The packing of this compound is directed by N−H···N hydrogen bonds and van der Waals contacts (Table 7). Through the first ones, we can distinguish a secondary structure of chains that extend along the **c** axis and are strengthen by T-shaped interactions between (C11, ..., C16) phenyl rings, with interplanar angles of 67.9(5)° (Figure 2). These chains are joined through two different van der Waals contacts to give a tertiary structure of layers (100); one of both forms T-shaped chains along the b axis with aromatic interplanar angles of 61.8(5)°, and the other contact forms parallel stacked dimers with parameters $d(z) = 3.53$ Å and $d(xy) = 2.10$ Å (distance between the ring planes and the separation in projection of the two centroids, respectively).[57] Finally, the crystal forms by the joining the layers through a slack T-shaped interaction, where the C6−H6 bond of one molecule points toward the imidazole ring of other one; the observed interplanar angle is 58.5(4)°. There are no voids in the structure, and the total packing coefficient is 0.69.[58]

Comparative Survey of Enthalpies of Formation

As mentioned in the Introduction, the possible existence of correlations between the enthalpies of formation of series of related compounds bearing the same kind of substituents can be very useful to have reasonably good estimates of the enthalpies of formation for other series of compounds for which this information is not available, from calculated values obtained from suitable atom equivalent schemes. In a series of five papers,[1−5] we have reported experimental and calculated en-

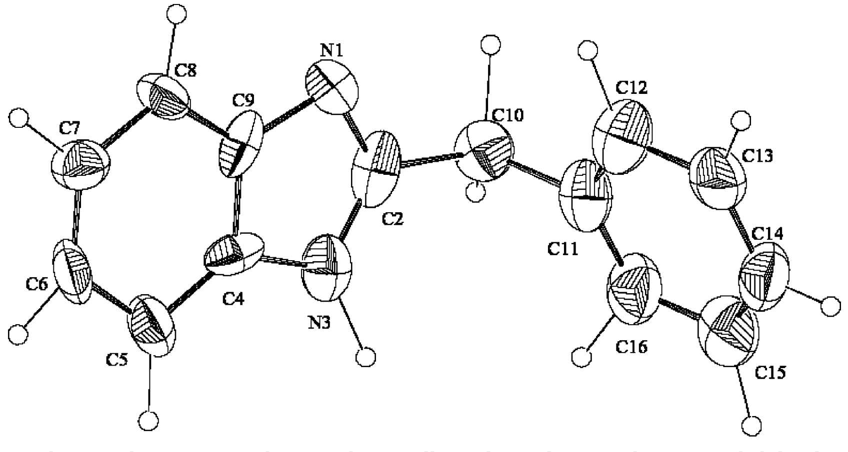


Figure 1. Molecular structure showing the atomic numbering scheme. Ellipsoids are drawn at the 30% probability level for non-H atoms, and the hydrogen atoms are denoted as spheres of 0.1 Å radii.

TABLE 6: Selected Geometrical Parameters (Distances, Å; Angles, deg)

N1−C2	1.34(3)	C7−C8	1.44(2)	C11−C12	1.37(3)
C2−N3	1.33(2)	C8−C9	1.38(2)	C12−C13	1.42(3)
N3−C4	1.41(2)	N1−C9	1.40(2)	C13−C14	1.39(3)
C4−C5	1.41(2)	C4−C9	1.38(3)	C14−C15	1.37(3)
C5−C6	1.37(2)	C2−C10	1.53(2)	C15−C16	1.42(3)
C6−C7	1.36(3)	C10−C11	1.54(2)	C11−C16	1.37(3)
C2−N1−C9	106(1)	C6−C7−C8	124(2)	C10−C11−C16	117(2)
N1−C2−N3	117(1)	C7−C8−C9	111(1)	C12−C11−C16	125(2)
C2−N3−C4	99(1)	C4−C9−C8	125(2)	C11−C12−C13	117(2)
N3−C4−C9	115(1)	N1−C2−C10	123(2)	C12−C13−C14	119(2)
N1−C9−C4	103(1)	N3−C2−C10	120(2)	C13−C14−C15	123(2)
C5−C4−C9	121(2)	C2−C10−C11	113(1)	C14−C15−C16	118(2)
C4−C5−C6	116(1)	C10−C11−C12	117(2)	C11−C16−C15	118(2)
C5−C6−C7	122(2)				
C4−N3−C2−C10	−177(1)	N3−C2−C10−C11	99(2)		
C2−C10−C11−C12	−74(2)	C10−C11−C12−C13	−179(2)		

TABLE 7: Geometry of Hydrogen Bonds (Distances, Å; Angles, deg)[a]

	D−H	H···A	D···A	D−H···A
N1−H1···N3 $(x, \frac{1}{2} - y, \frac{1}{2} + z)$	1.29(9)	1.57(9)	2.81(2)	159(7)
C12−H12···C1116 $(x, \frac{1}{2} - y, z - \frac{1}{2})$	1.21(12)	2.97(11)	4.09(2)	154(6)
C14−H14···C0409 $(-x, y + \frac{1}{2}, \frac{3}{2} - z)$	1.07(12)	2.71(12)	3.64(2)	145(8)
C1116···C1116 $(-x, 1 - y, 1 - z)$			4.11(1)	
C6−H6···C0109 $(\frac{1}{2} - x, y - \frac{1}{2}, z)$	1.15(12)	3.20(10)	3.78(2)	112(6)

[a] C0109, C0409 and C1116 represent the centroids of the rings (N1, C2, ..., C9), (C4, C5, ..., C9) and (C11, C12, ..., C16), respectively.

thalpies of formation for the five families of compounds included in Chart 2. The common feature of these five families is that they present the same kind of substituents attached to different aromatic moieties: benzene (**1**), imidazole (**2**, **3**), pyrazoles (**4**) and benzimidazole (**5**). Both experimental and calculated values are summarized in Table 8. It is worth noting that the 10 values in italics (*N*-propyl-, *N*-isopropyl-, *N*-*tert*-butyl- and one *N*-benzylimidazoles and pyrazoles) have not been measured but estimated from linear regression between calculated and experimental values (see further discussion in Table 9). The full correlation matrix, including these values, i.e., the eight substituents for the five families, is also reported in Table 8.

The first finding is that, for each family of compounds there is a very good correlation between experimental and calculated values with correlation coefficients (in bold in the correlation matrix) close to unity. The second important finding is that both calculated and experimental values are internally consistent independently of the R groups being attached to C or N. The worse correlation coefficients are those of **3** vs **2** [(0.969 (exp), 0.986 (calc)], **4** vs **5** [0.983 (exp), 0.989 (calc)], and **3** vs **5** [0.958 (exp), 0.983 (calc)], which correspond to N- vs C-substituted compounds. On the other side, the correlation between 2-substituted benzimidazoles **5** and 2-substituted imidazoles **2** is very good [0.990 (exp), 1.000 (calc.)]. That shows that the effect of R is not fully independent of the ring that bears it.

Figure 3 is a plot of experimental vs calculated values for 2R−benzimidazoles **5**.

To the second equation of Figure 3 corresponds the following residuals −6.9 (R = H), −7.1 (R = CH_3), −13.4 (R = C_2H_5), +8.9 (R = C_3H_7), −3.9 (R = *i*-C_3H_7), +10.1 (R = *t*-C_4H_9), +7.7 (R = $CH_2C_6H_5$) and + 4.4 kJ mol^{-1} (R = C_6H_5). What is the origin of the larger residuals of the ethyl and *tert*-butyl groups? If the error source were the experimental results, one would expect that they would be at random, i.e., independent of the substrate. On the contrary, if they are related to the calculations, the expectation is that they will be related to one particular substituent.

In the case of the benzene derivatives, $\Delta_f H^o(\text{exp}) = (1.16 \pm 0.05)\Delta_f H^o(\text{calc}) + (2.4 \pm 4.1)$ kJ mol^{-1}, $n = 8$, $r^2 = 0.988$. In

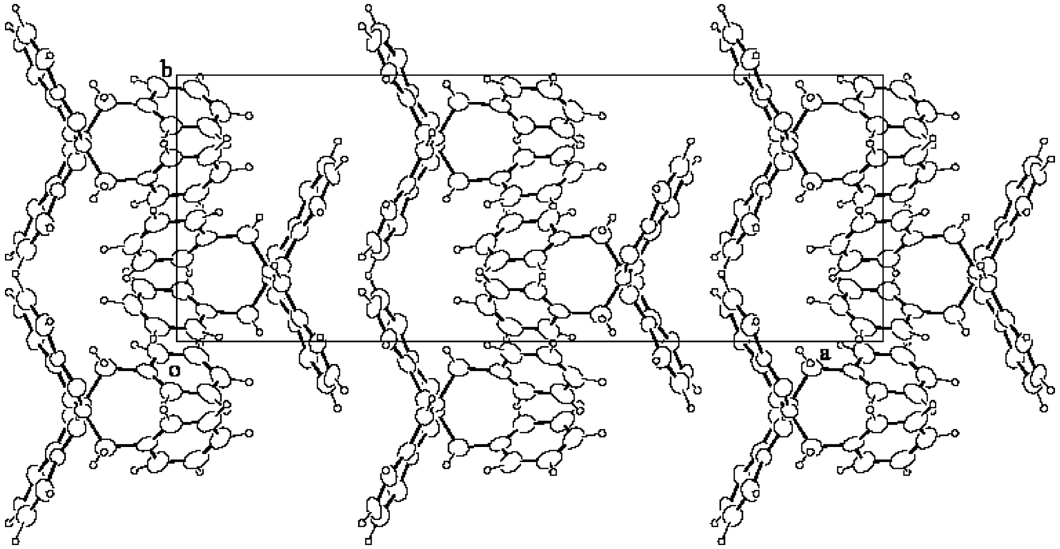


Figure 2. Crystal packing diagram as projected along the **c** axis.

TABLE 8: Enthalpies of Formation of Compounds 1−5 (kJ mol^{-1})

Experimental Data

R	benzene **1**	2R−imid **2**	1R−imid **3**	1R−pyraz **4**	2R−benzimid **5**
H	82.6	132.9	132.9	179.4	181.7
CH_3	50.0	89.1	137.8	156.5	129.5
C_2H_5	29.8	68.3	110.8	132.6	114.0
C_3H_7	7.8	*53.0*	*88.9*	*97.6*	63.2
i-C_3H_7	3.9	*53.2*	*84.6*	*104.3*	78.3
t-C_4H_9	−22.7	*37.6*	*68.3*	*90.0*	43.3
CH_2Ph	164.8	*189.5*	244.1	276.6	239.2
Ph	182.0		264.7	291.4	258.0

Calculated

R	benzene **1**	2R−imid **2**	1R−imid **3**	1R−pyraz **4**	2R−benzimid **5**
H	63.6	145.4	145.4	190.0	188.4
CH_3	36.4	105.4	140.0	179.0	146.3
C_2H_5	18.7	88.4	115.0	151.0	127.5
C_3H_7	−0.6	68.8	98.0	121.0	109.1
i-C_3H_7	2.0	69.0	94.0	127.0	108.4
t-C_4H9	−7.0	52.9	79.0	115.0	94.3
CH_2Ph	145.0	209.7	243.0	280.0	249.2
Ph	154.0	219.7	257.0	295.0	261.0

Correlation Matrix (Including the Predicted Values in Italics)

	1 exp	**2** exp	**3** exp	**4** exp	**5** exp	**1** calc	**2** calc	**3** calc	**4** calc	**5** calc
1 exp	1	0.994	0.987	0.995	0.988	**0.994**	0.997	0.992	0.993	0.996
2 exp		1	0.969	0.990	0.990	0.992	**0.999**	0.979	0.986	0.999
3 exp			1	0.991	0.958	0.989	0.977	**0.999**	0.994	0.993
4 exp				1	0.983	0.998	0.994	0.995	**0.999**	0.993
5 exp					1	0.977	0.991	0.967	0.979	**0.991**
1 calc						1	0.995	0.994	0.996	0.994
2 calc							1	0.986	0.991	1.000
3 calc								1	0.997	0.983
4 calc									1	0.989
5 calc										1

this case also the *tert*-butyl group shows the largest residual (−17.0 kJ mol^{-1}). This seems to indicate that for some reason the theoretical methods underestimate the intrinsic stability of compounds with bulky substituents. To fully confirm this conclusion, it would be necessary to gather information of the heats of formation with an increasing number of families bearing the same bulky substituents.

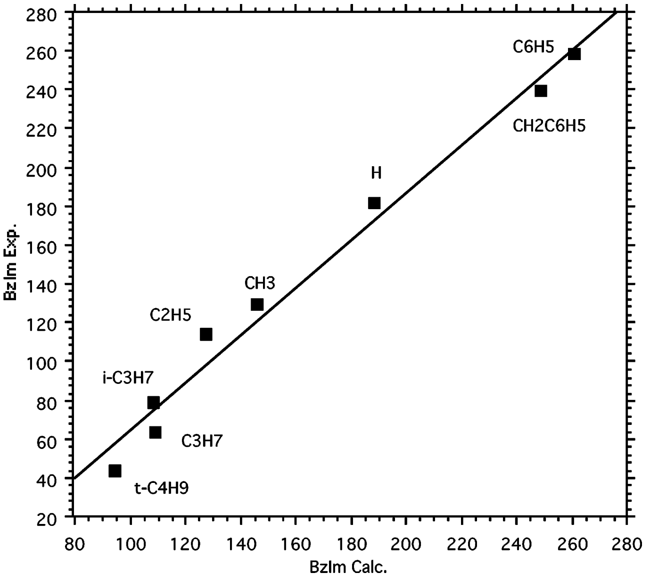


Figure 3. Linear correlation between experimental enthalpies of formation and calculated values for 2-substituted benzimidazoles **5** (values in kJ mol^{-1}). The linear correlation obeys the equation $\Delta_fH°(\text{exp}) = (1.22 \pm 0.07)\Delta_fH°(\text{calc}) - (58 \pm 12)$ kJ mol^{-1}, $n = 8$, $r = 0.991$, $r^2 = 0.982$. Reciprocally, $\Delta_fH°(\text{calc}) = (0.80 \pm 0.04)\Delta_fH°(\text{exp}) + (49 \pm 7)$ kJ mol^{-1}, $n = 8$, $r = 0.991$.

A possible explanation for the relative differences between calculated and experimental values, i.e., why some compounds deviate more than some others, is related to the conformational effects. The calculated values correspond to the minimum energy conformation and the experimental ones are obtained at 298.15 K from a mixture of conformations, weighted according to their relative energies. This effect should impact conformationally rich compounds more than simpler ones, like those with R = H or R = CH_3.

The whole collection of relationships is reported in Table 9 (eqs 7−21).

We then decided to apply the knowledge already gathered to predict the enthalpies of formation of indazoles **6** and **7**. For 3-substituted indazoles we have calculated only the 1*H*-tautomer **6** because it is known to be much more stable than the 2*H*.[59] The only known value is the data for indazole itself (R = H), $\Delta_fH^o_{\text{gas}} = 243.0 \pm 1.3$ kJ mol^{-1}.[1] The calculated values are reported in Table 10.

By obvious structural analogy, for set **6** we have selected eq 21 that holds for 2-substituted benzimidazoles, and for set **7** eq 20 that holds for N-substituted pyrazoles (the calculated values of **6**/**5** and **7**/**4** pairs are highly correlated, in both cases $r^2 = 0.998$). With these equations we obtained for indazole itself (R = H) a value slightly above and slightly below, respectively, the experimental value, reflecting the fact already mentioned that substituent effects are not strictly transferable from one family of compounds to another. Nevertheless, the difference between both estimates is small enough to give us confidence that the calculated values shown in the two right columns of Table 10 are reasonable estimations of the true, still unknown, experimental values of 14 indazoles.

TABLE 9: Correlation Equations (kJ mol^{-1}), Always $n = 8$ Data

Experimental vs Experimental	
$\mathbf{2} = (0.83 \pm 0.04)\,\mathbf{1} + (51 \pm 3)$, $r^2 = 0.988$	(7)
$\mathbf{3} = (0.96 \pm 0.06)\,\mathbf{1} + (82 \pm 6)$, $r^2 = 0.973$	(8)
$\mathbf{4} = (1.04 \pm 0.04)\,\mathbf{1} + (102 \pm 4)$, $r^2 = 0.991$	(9)
$\mathbf{5} = (1.05 \pm 0.07)\,\mathbf{1} + (73 \pm 6)$, $r^2 = 0.977$	(10)
$\mathbf{3} = (1.13 \pm 0.12)\,\mathbf{2} + (25 \pm 14)$, $r^2 = 0.938$	(11)
$\mathbf{4} = (1.24 \pm 0.07)\,\mathbf{2} + (39 \pm 9)$, $r^2 = 0.980$	(12)
$\mathbf{5} = (1.26 \pm 0.07)\,\mathbf{2} + (9 \pm 8)$, $r^2 = 0.977$	(13)
$\mathbf{4} = (1.06 \pm 0.06)\,\mathbf{3} + (16 \pm 9)$, $r^2 = 0.983$	(14)
$\mathbf{5} = (1.04 \pm 0.13)\,\mathbf{3} + (9 \pm 20)$, $r^2 = 0.918$	(15)
$\mathbf{5} = (1.00 \pm 0.08)\,\mathbf{4} - (28 \pm 14)$, $r^2 = 0.966$	(16)
Experimental vs Calculated (Cioslowski)	
$\mathbf{1}$ exp $= (1.16 \pm 0.05)\,\mathbf{1}$ calcd $- (2 \pm 4)$, $r^2 = 0.988$	(17)
$\mathbf{2}$ exp $= (0.97 \pm 0.02)\,\mathbf{2}$ calcd $- (14 \pm 2)$, $r^2 = 0.998$	(18)
$\mathbf{3}$ exp $= (1.09 \pm 0.02)\,\mathbf{3}$ calcd $- (17 \pm 3)$, $r^2 = 0.998$	(19)
$\mathbf{4}$ exp $= (1.12 \pm 0.02)\,\mathbf{4}$ calcd $- (38 \pm 3)$, $r^2 = 0.999$	(20)
$\mathbf{5}$ exp $= (1.22 \pm 0.07)\,\mathbf{5}$ calcd $- (58 \pm 12)$, $r^2 = 0.982$	(21)

TABLE 10: Calculated Enthalpies of Formation of Indazoles (kJ mol^{-1})

R	3-substituted indazoles **6**	1-substituted indazoles **7**	predicted **6** (eq 21, Table 7)	predicted **7** (eq 20, Table 7)
H	249.6	249.6	246.8	241.8
CH_3	211.9	238.0	200.8	228.8
C_2H_5	196.6	212.2	182.2	199.9
C_3H_7	178.3	193.2	159.8	178.6
i-C_3H_7	178.9	188.8	160.6	173.7
t-C_4H9	166.3	182.2	145.2	166.3
CH_2Ph	319.8	340.6	332.5	343.7
Ph	333.3	357.8	348.9	362.9

TABLE 11: Enthalpies (kJ mol^{-1}) of Sublimation of 2R−Benzimidazoles (Kem, Knudsen-Effusion Method; CMc, Calvet Microcalorimetry) and Some Crystallographic Data (Distances, Å; Densities, Mg m^{-3})

R	$\Delta_{cr}^{g}H_{m}^{o}$	method	ref	d_{NN}	density	refcode[a]
H	102.2 ± 0.4	Kem	1	2.85	1.232	BZDMAZ02
CH_3	102.6 ± 0.8	Kem	2	2.91	1.255	KOWYEA
C_2H_5	107.6 ± 2.1	CMc	2	not reported	1.179	ETBZIM
C_3H_7	109.4 ± 1.1	Kem	3			
i-C_3H_7	109.9 ± 2.7	CMc	3			
t-C_4H_9	115.1 ± 2.9	CMc	*b*			
CH_2Ph	136.2 ± 0.5	Kem	4	2.81	1.218	this work
Ph	123.0 ± 1.7	CMc	4	2.80	1.223	submitted[66]

[a] From the Cambridge Structural Database.[65] [b] Table S5.

Relationship between Calorimetry and X-ray Molecular Structure

It is not the aim of this paper to made a significant contribution to the difficult problem of lattice energies,[60] crystal density,[61,62] and enthalpies of sublimation.[63,64] Ouvrard and Mitchell have published an important paper on lattice energy (enthalpies of sublimation $= -E_{\text{lattice}} - 2RT$).[64] They propose several models to relate $\Delta_{cr}^{g}H_{m}^{o}$/kJ mol^{-1} to the molecular structure. Following these authors, we have treated the data of Table 11 in different ways.

$$\Delta_{cr}^{g}H^{\circ}_{m}/\text{kJ mol}^{-1} = (4.6 \pm 0.5) \times \text{no. of C atoms} + (66 \pm 6) \qquad n = 8,\ r^2 = 0.92 \quad (22)$$

$$\Delta_{cr}^{g}H^{\circ}_{m}/\text{kJ mol}^{-1} = (0.36 \pm 0.05) \times \text{MW} + (55 \pm 8) \qquad n = 9,\ r^2 = 0.90 \quad (23)$$

Differentiating sp^2 and sp^3 carbons, as has been proposed,[65] does not improve eq 22. With eq 22, the largest residuals are found for **BIM** (+4.0, fitted 98.2 kJ mol^{-1}) and for **2BnBIM** (+5.6, fitted 130.6 kJ mol^{-1}). We have tried to relate the enthalpies of sublimations to some molecular crystal properties (Table 11). First, it is interesting to point out that the density and the N···N distance are related (eq 24).

$$\text{density} = (0.32 \pm 0.05) \times d_{NN} + (0.32 \pm 0.15) \qquad n = 4,\ r^2 = 0.95 \quad (24)$$

Again, the maximum deviation is found for **2BnBIM**. The positive slope is counterintuitive because one expects that shorter N···N distances correspond to denser compounds. The attempts to correlate enthalpies of sublimation with densities or N···N distances were disappointing. It seems clear that more structures need to be determined before going further.

It is worth noting, however, that by the simple method of counting the number of H and C atoms of the substituents, one obtains for enthalpies of formation:

$$\Delta_f H(\text{Table 10}) = (210 \pm 9) - (36 \pm 2) \times \text{no. of H} + (39 \pm 2) \times \text{no. of C} \qquad n = 8,\ r^2 = 0.99 \quad (25)$$

If, instead of the number of H and C of the substituent, we use the whole molecule (molecular formula), obviously only the intercept changes (because it corresponds to add a C_7H_5 fragment):

$$\Delta_f H(\text{Table 10}) = (115 \pm 17) - (36 \pm 2) \times \text{no. of H} + (39 \pm 2) \times \text{no. of C} \qquad n = 8,\ r^2 = 0.99 \quad (26)$$

Finally, it is worth mentioning that although, as discussed in this section, **2BnBIM** deviates in the correlation between enthalpies of formation and the number of C atoms, as well as in the correlation between density and N···N distances, its experimental enthalpy of formation cannot be under suspicion because it is perfectly consistent with the corresponding calculated value. Therefore, the anomaly is probably related to its low density, but more structures of 2-substituted benzimidazoles will be necessary to understand these deviations that, as a matter of fact, are minor.

Concluding Remarks

From our experimental and theoretical survey of the substituent effects on the enthalpies of formation of five different families of nitrogen-containing aromatic compounds we can conclude that substituent effects are not strictly transferable from one family to another, as they seem to depend on the nature of the cycle to which they are attached. Nevertheless, both calculated and experimental values are internally consistent in the sense that the correlation between enthalpies of formation of the different families is in general reasonably good. Systematically, the poorer correlations are found for those cases in which the substituent is attached to a different atom (C or N) of the aromatic moiety, but even in these cases the correlation coefficient is never smaller than 0.969.

The existence of these reasonably good correlations opens the possibility of estimating the enthalpies of formation for other families of closely related compounds. This has been applied in the present paper for two families of nitrogen containing aromatic systems, namely 1- and 3-susbtituted indazoles.

In general, very good correlations have been found between experimental and calculated values obtained through the use of appropriate atom equivalent techniques.

Also interestingly, a quite good correlation seems to exist between enthalpies of formation and the number of C and H atoms of the substituents.

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Supporting Information Available: Table S1 to Table S7 listing details of the Knudsen effusion cells, crystal data and structure determination details for **2BnBIM,** results of the experimental determination of the massic energies of combustion of 2-*tert*-butylbenzimidazole (**2*t*BuBIM**) and 2-phenylimidazole (**2PhIM**), results of the microcalorimetry sublimation experiments of 2-*tert*-butylbenzimidazole, and Knudsen effusion results of 2-phenylimidazole and molar heat capacities at different temperatures of 2-*tert*-butylbenzimidazole. This material is available free of charge via the Internet at http://pubs.acs.org

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