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Standard molar enthalpies of formation of 5- and 6-nitroindazole

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Abstract The present work reports the experimental determination of the standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation in the condensed and gaseous phases, at $T = 298.15$ K, of 5- and 6-nitroindazole. These results were derived from the measurements of the standard molar energies of combustion, using a static bomb calorimeter and from the standard molar enthalpies of sublimation derived by the application of Clausius–Clapeyron to the temperature dependence of the vapour pressures measured by the Knudsen effusion technique. The results are interpreted in terms of the energetic contributions of the nitro groups in the different positions of the aromatic ring.

Keywords Combustion calorimetry · Knudsen effusion technique · 5-Nitroindazole · 6-Nitroindazole · Enthalpy of combustion · Enthalpy of sublimation · Enthalpy of formation

Introduction

Although indazoles are rare in the nature [1], a considerable attention has been paid to the chemistry of this class of compounds, due to its biological activity, mainly in enzymatic systems. The molecular shape and electrostatic distribution play an important role in enzyme and receptor recognition and contribute to binding affinity. The determination of physical and chemical properties of indazoles has been the object of many studies in order to contribute to the development of new pharmaceutical drugs [2].

A particular case of important indazoles derivates are the nitroindazoles. These compounds are considered a unique class of nitric oxide syntheses inhibitors. Since nitric oxide is a key signalling molecule in many biological processes, the regulation and monitoring of nitric oxide levels is very important in human physiology and medicine [3]. Nitroindazoles and their derivates were also identified as good anti-parasites, particularly against pathogenic protozoa such as *Tripanosoma cruzi*, a considerable worldwide health problem [4–6]. The high biological activity of indazoles can cause them to interact with organic systems forming toxic intermediates, conferring these compounds mutagenic and carcinogenic properties; several studies have been carried out to confirm these features [7].

The present work reports the study of the thermochemical properties of two nitroindazoles, the 5- and 6-nitroindazole whose structure is presented in Fig. 1.

The standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation in the condensed phase were derived from the respective standard massic energies of combustion, measured by static bomb combustion calorimetry, while the standard molar enthalpies of sublimation, at $T = 298.15$ K, were derived from the variation of the vapour pressure with the temperature, measured by the Knudsen effusion technique and the application of the Clausius–Clapeyron equation. From these two sets of results, the standard molar enthalpies of formation in the gaseous state, at $T = 298.15$ K, were derived.

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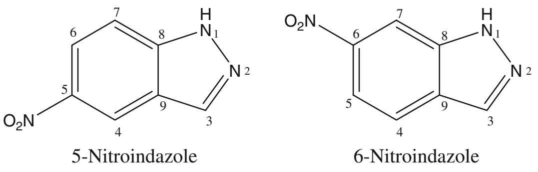


Fig. 1 Structural formula for 5-nitroindazole and 6-nitroindazole

Experimental

Compounds and purity control

The 5-nitroindazole [CAS 5401-94-5] and 6-nitroindazole [CAS 7597-18-4] were obtained commercially from Aldrich Chemical Co with initial purity of 0.97 mass fractions for both compounds. They were purified twice by sublimations under reduced pressure and the final purity was confirmed by GLC and determined recovering the carbon dioxide produced in the combustion experiments. The average ratios of the mass of carbon dioxide recovered after combustion, to that calculated from the mass of sample, were (1.00036 ± 0.00003) and (1.00007 ± 0.00024), respectively, for 5- and 6-nitroindazole, where the uncertainties are the standard deviations of the means.

Combustion calorimetry

The standard molar energies of combustion of the compounds under study were measured using an isoperibol calorimeter equipped with a static combustion bomb, type 1105, Parr Instruments Company, made of stainless steel and with an internal volume of 0.340 cm^3. The apparatus and procedure followed has been previously described [8, 9].

The calibration of the calorimeter was done by combustion of Thermochemical Standard benzoic acid, sample NBS 39j, with massic energy of combustion, under bomb conditions, of $\Delta_c u = -(26434 \pm 3)$ J g^{-1} [10], and corrected to give the energy equivalents, ε_{cal}, corresponding to the average mass of water added to the calorimeter, 3119.6 g. From six calibration experiments, $\varepsilon_{cal} = (15917.4 \pm 1.4)$ J K^{-1}, using the calibration procedure as described by Coops et al. [11]. The uncertainties quoted are the standard deviations of the mean.

In all the experiments, 1.00 cm^3 of water was added to the bomb and the crystalline compounds were burnt in pellet form, into a platinum crucible. Since both studied compounds have explosive properties and do not burn completely, it was necessary to use paraffin oil (Aldrich Gold Label, mass fraction > 0.999), stored under nitrogen, or melinex, as combustion auxiliaries. The massic energy of combustion of this sample of paraffin oil was measured in our laboratory and was found to be $\Delta_c u$ (paraffin oil) = $-(47193.3 \pm 3.3)$ J g^{-1}. For melinex the value $\Delta_c u$ (melinex) = $-(22902 \pm 5)$ J g^{-1}, published by Skinner and Snelson [12] and confirmed in our Laboratory, was used. The combustion bomb was flushed and filled with oxygen to the pressure of 3.04 MPa and the ignition was made at $T = (298.150 \pm 0.001)$ K, by the discharge of a 1400 μF capacitor through the platinum ignition wire, and using a cotton-thread fuse of empirical formula $CH_{1.686}O_{0.843}$, with $\Delta_c u^{o}$ (fuse) = $-(16250)$ J g^{-1} [11], a value which was confirmed in our Laboratory. The electrical energy of ignition was determined from the change of potential across the capacitor. The calorimeter temperatures were measured to $\pm(1 \times 10^{-4})$ K, at time intervals of 10 s, with a quartz crystal thermometer (Hewlett Packard HP 2804A), interfaced to a PC. 100 readings were taken for the main period and for both the fore and after periods. At the end of each experiment, the amount of compound burnt in that experiment was determined from the total mass of CO_2 produced during the combustion experiment, taking into account that formed from the combustion of the cotton-thread fuse, the paraffin oil or the melinex, and that lost due to eventual carbon formation. For that, the gases in the bomb, at the end of the experiment, were driven through CO_2 recovering tubes, filled with Carbosorb AS self-indicating, and previously weighed. The amount of HNO_3 formed was determined by titration of the aqueous solution resulting from washing the inside of the bomb.

Knudsen effusion technique

For the crystalline compounds 5- and 6-nitroindazole, the vapour pressures were measured at several temperatures, using a Knudsen mass-loss effusion apparatus, enabling the simultaneous operation of nine effusion cells at three different temperatures. Detailed description of the apparatus, procedure, and the technique used has been described [13].

For each compound, the temperature interval was chosen so that the vapour pressures were measured in the range 0.1–1.0 Pa. In each effusion experiment, the mass loss, Δm, during the effusion period, t, is determined by weighing the effusion cells in a Mettler AE 163 balance, sensitivity ±0.01 mg, before and after the effusion time in a system evacuated to a pressure near (1×10^{-4}) Pa. At the temperature T of the experiment, the vapour pressure p is calculated by the Knudsen equation (Eq. 1):

$$p = \left(\frac{\Delta m}{A_o w_o t}\right)\sqrt{\frac{2\pi RT}{M}}, \tag{1}$$

where M is the molar mass of the effusing vapor, R is the gas constant, A_o is the area of the effusion orifice, and w_o is the respective Clausing factor calculated by Eq. 2, where l is the thickness of the effusion orifice and r its radius:

$$w_o = \left\{1 + \left(\frac{3l}{8r}\right)\right\}^{-1}. \tag{2}$$

The thickness of the effusion orifices was 0.0125 mm, and their areas and Clausing factors are registered in Table 1.

Results

The detailed results of each combustion experiment, the mean values of the massic energies of combustion, $\langle \Delta_c u^o \rangle$ and the respective deviations for 5- and 6-nitroindazole are given in Tables 2 and 3, respectively, where $\Delta m(H_2O)$ is the deviation of the mass of water added to the calorimeter from 3119.6 g, with the internal energy for the isothermal bomb process, $\Delta U(\text{IBP})$, calculated according to the Eq. 3:

$$\Delta U(\text{IBP}) = -\{\varepsilon_{\text{cal}} + \Delta m(H_2O) \cdot C_p(H_2O, 1) + \varepsilon_f\}\Delta T_{\text{ad}} + \Delta U(\text{ign}). \tag{3}$$

Table 1 Areas and transmission probability factors of the effusion orifices

	Orifice number	A_o/mm^2	w_o
Small orifices	A1	0.502	0.988
	A2	0.509	0.988
	A3	0.523	0.988
Medium orifices	B4	0.774	0.991
	B5	0.783	0.991
	B6	0.792	0.991
Large orifices	C7	1.019	0.992
	C8	1.125	0.992
	C9	1.131	0.992

$\Delta U(\text{fuse})$ is the energy of combustion of the cotton-thread fuse, $\Delta U(\text{Aux})$ is the combustion energy of the combustion auxiliary, $\Delta U(\text{ign})$ is the electrical energy supplied for ignition, $\Delta U(HNO_3)$ is the correction for the nitric acid formation, based on -59.7 kJ mol^{-1}, for the molar energy of formation of a 0.1 mol dm^{-3} solution of HNO_3 (aq), from N_2 (g), O_2 (g), and H_2O (l) [14], ΔU_Σ is the correction to the standard state calculated by the procedure of Hubbard et al. [15] and $\Delta_c u^o$ is the massic energy of combustion of the compound, calculated as previously described [15].

An estimated massic energy pressure coefficient, $(\partial u/\partial p)_T$, at $T = 298.15$ K, was assumed to be -0.2 J g^{-1} MPa^{-1}, a typical value for most organic compounds [16]. The atomic masses of the elements were those recommended by the IUPAC Commission in 2005 [17].

Table 4 lists the derived standard molar values for the energies, $\Delta_c U^o_m$, and enthalpies, $\Delta_c H^o_m$, of combustion, referred to the combustion reaction of 5- and 6-nitroindazole, according to Eq. 4

$$C_7H_5N_3O_2(\text{cr}) + \frac{29}{4}O_2\,(\text{g}) \rightarrow 7\ CO_2\,(\text{g}) + \frac{5}{2}H_2O\ (\text{l}) + \frac{3}{2}N_2\,(\text{g}). \tag{4}$$

Table 2 Results of the combustion experiments of 5-nitroindazole, at $T = 298.15$ K

Experiment	1	2	3	4	5	6
$m(CO_2, \text{total})/\text{g}$	–	–	1.61846	1.60077	1.43858	1.58039
$m(\text{cpd})/\text{g}$	0.46963	0.65056	0.66570	0.63047	0.57779	0.64880
$m(\text{fuse})/\text{g}$	0.00302	0.00287	0.00266	0.00303	0.00298	0.00298
$m(\text{Aux})/\text{g}$	–	0.10849[b]	0.11499[b]	0.13033[b]	0.11019[b]	0.11267[b]
$\Delta T_{\text{ad}}/\text{K}$	0.65327	1.22600	1.26509	1.26323	1.13038	1.23629
$\varepsilon_f/\text{J K}^{-1}$	15.04	15.65	15.74	15.78	15.61	15.78
$\Delta m(H_2O)/\text{g}$	0.0	+0.1	+0.1	−0.1	+0.1	0.0
$-\Delta U(\text{IBP})$[a]$/\text{J}$	10407.51	19533.53	20156.52	20126.04	18010.17	19697.37
$\Delta U(\text{fuse})/\text{J}$	49.04	46.61	43.20	49.21	48.40	48.40
$\Delta U(\text{Aux})/\text{J}$	–	5116.42	5422.86	6146.22	5196.22	5313.32
$\Delta U(HNO_3)/\text{J}$	35.28	62.69	60.30	58.45	53.97	56.95
$\Delta U(\text{ign})/\text{J}$	0.68	0.90	0.87	0.70	0.66	0.66
$-\Delta U(\text{carbon})/\text{J}$	–	–	4.95	–	–	–
$\Delta U_\Sigma/\text{J}$	9.91	15.17	15.65	15.07	13.60	15.27
$-\Delta_c u^o/\text{J g}^{-1}$	21960.44	21969.75	21961.03	21978.98	21976.81	21984.32
% CO_2	(100.036)	(100.036)	100.035	100.029	100.044	100.036

$\langle \Delta_c u^o \rangle = -(21971.9 \pm 4.0)\ \text{J g}^{-1}$

[a] $\Delta U(\text{IBP})$ already includes the $\Delta U(\text{ign})$

[b] Paraffin oil as combustion auxiliary

Table 3 Results of the combustion experiments of 6-nitroindazole, at $T = 298.15$ K

Experiment	1	2	3	4	5	6
$m(CO_2$, total)/g	1.35814	1.58505	1.60454	–	1.35773	1.63963
m (cpd)/g	0.67449	0.58078	0.64059	0.57252	0.51510	0.65004
m(fuse)/g	0.00297	0.00256	0.00245	0.00278	0.00237	0.00251
m(Aux)/g	0.03476[c]	0.15569[b]	0.12602[b]	0.12554[b]	0.12281[b]	0.13163[b]
ΔT_{ad}/K	0.98950	1.27030	1.26608	1.16961	1.08190	1.29533
ε_f/J K^{-1}	15.22	15.60	15.73	15.71	15.61	15.81
$\Delta m(H_2O)$/g	0.0	+0.1	+0.1	0.0	0.0	0.0
$-\Delta U$(IBP)[a]/J	15764.34	20239.18	20172.44	18634.34	17237.24	20638.08
ΔU(fuse)/J	48.23	41.57	39.79	45.15	38.49	40.76
ΔU(Aux)/J	796.14	7347.66	5947.11	5924.43	5795.91	6212.20
$\Delta U(HNO_3)$/J	58.51	57.79	68.06	51.82	48.36	65.07
ΔU(ign)/J	0.99	1.04	0.71	1.18	0.68	0.68
$-\Delta U$(carbon)/J	–	–	8.91	15.18	–	11.88
ΔU_Σ/J	15.02	14.27	15.10	13.73	12.39	15.46
$-\Delta_c u^o$/J g^{-1}	22011.36	22001.26	22028.58	22033.10	22019.20	22023.98
% CO_2	100.076	100.007	100.019	(100.007)	99.926	100.006
$\langle\Delta_c u^o\rangle = -(22019.6 \pm 4.8)$ J g^{-1}						

$m(CO_2)$ is the mass of CO_2 recovered in the 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(Aux) is the mass of combustion auxiliary used, paraffin oil or melinex, ΔT_{ad} is the corrected temperature rise, ε_f is the energy equivalent of contents in the final state, $\Delta m(H_2O)$ 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(Aux) is the energy of combustion of the auxiliary, $\Delta U(HNO_3)$ is the energy correction for the nitric acid formation, ΔU(ign) is the electrical energy for ignition, ΔU(carbon) is the massic energy correction for the carbon soot residue, ΔU_Σ is the standard state correction, $\Delta_c u^o$ is the standard massic energy of combustion

[a] ΔU(IBP) already includes the ΔU(ign), [b] paraffin oil as combustion auxiliary, [c] melinex as combustion auxiliary

Table 4 Condensed phase standard ($p^\circ = 0.1$ MPa) molar thermochemical functions at $T = 298.15$ K

Compound	$-\Delta_c U_m^o$/kJ mol^{-1}	$-\Delta_c H_m^o$/kJ mol^{-1}	$\Delta_f H_m^o$(cr)/kJ mol^{-1}
5-Nitroindazole	3584.4 ± 1.5	3581.3 ± 1.5	112.2 ± 1.8
6-Nitroindazole	3592.1 ± 1.8	3589.0 ± 1.8	119.9 ± 2.0

The uncertainties of the standard molar energies and enthalpies of combustion are twice the final overall standard deviation of the mean, and include the uncertainties in calibration [18, 19].

The values of the standard molar enthalpies of formation in the condensed phase, $\Delta_f H_m^o(\mathrm{cr})$, also registered in Table 4, were derived from $\Delta_c H_m^o$, using the values, at $T = 298.15$ K, of the standard molar enthalpies of formation of liquid water and gaseous carbon dioxide, respectively, as $\Delta_f H_m^o(H_2O,\ l) = -(285.830 \pm 0.042)\ \mathrm{kJ\,mol^{-1}}$ [20] and $\Delta_f H_m^o(CO_2,\ g) = -(393.51 \pm 0.13)\ \mathrm{kJ\,mol^{-1}}$ [20].

The integrated form of the Clausius–Clapeyron equation, $\ln(p/\mathrm{Pa}) = a - b\ (T/\mathrm{K})^{-1}$, where a is a constant and $b = \frac{\Delta_{cr}^{g} H_m^o(\langle T\rangle)}{R}$, was used to derive the standard molar enthalpies of sublimation, at the mean temperature of the experimental temperature range. The experimental results obtained from each effusion cell, together with the residuals of the Clausius–Clapeyron equation, derived from the least squares adjustment, are registered in Tables 5 and 6, for 5- and 6-nitroindazole, respectively.

For each compound, the calculated enthalpies of sublimation obtained from each individual hole are in agreement within experimental error.

Table 7 presents for each hole used and for the global treatment of all the (p, T) points obtained for each studied compound, the detailed parameters of the Clausius–Clapeyron equation, together with the calculated standard deviation and the standard molar enthalpies of sublimation at the mean temperature of the experimental range $T = \langle T\rangle$. The equilibrium pressure at this temperature $p(T = \langle T\rangle)$ and the entropies of sublimation, at equilibrium conditions,

$$\Delta_{cr}^{g} S_m\{\langle T\rangle, p(T = \langle T\rangle)\} = \Delta_{cr}^{g} H_m^o(\langle T\rangle)/\langle T\rangle, \qquad (5)$$

are also registered in Table 7.

Table 5 Knudsen effusion results for 5-nitroindazole

T/K	*t*/s	Orifices	*p*/Pa			$10^2 \cdot \Delta\ln(p/Pa)$		
			p_A	p_B	p_C	p_A	p_B	p_C
377.127	23848	A1–B4–C7	0.2019	0.2014	0.1996	−0.2	−0.4	−1.3
379.266	23848	A2–B5–C8	0.2466	0.2465	0.2426	−0.8	−0.8	−2.4
381.184	23848	A3–B6–C9	0.3018	0.2957	0.2828	0.4	−1.6	−6.1
383.142	17987	A1–B4–C7	0.3808	0.3728	0.3772	4.9	2.8	3.9
385.175	17987	A2–B5–C8	0.4657	0.4585	0.4494	5.7	4.1	2.1
387.177	17987	A3–B6–C9	0.5579	0.5378	0.5324	4.9	1.2	0.2
389.139	12603	A1–B4–C7	0.6216	0.6386	0.6308	−2.6	0.1	−1.1
391.156	12603	A2–B5–C8	0.7390	0.7268	0.7208	−3.9	−5.5	−6.4
393.177	12603	A3–B6–C9	0.9056	0.8920	0.9047	−2.0	−3.5	−2.1
395.150	12191	A1–B4–C7	1.1388	1.0948	1.1337	3.1	−0.8	2.7
397.159	12191	A2–B5–C8	1.3641	1.3607	1.3094	3.2	2.9	−0.9
399.178	12191	A3–B6–C9	1.5977	1.5872	1.5547	1.1	0.5	−1.6

Table 6 Knudsen effusion results for 6-nitroindazole

T/K	*t*/s	Orifices	*p*/Pa			$10^2 \cdot \Delta\ln(p/Pa)$		
			p_A	p_B	p_C	p_A	p_B	p_C
359.119	24649	A1–B4–C7	0.1000	0.0998	0.0966	3.1	2.9	−0.3
361.159	24649	A2–B5–C8	0.1253	0.1213	0.1184	4.2	1.0	−1.5
363.182	24649	A3–B6	0.1493	0.1468	–	0.7	−1.0	–
365.135	19068	A1–B4–C7	0.1795	0.1781	0.1792	−1.0	−1.7	−1.1
367.170	19068	A2–B5–C8	0.2215	0.2216	0.2200	−0.6	−0.6	−1.3
369.183	19068	A3–B6–C9	0.2687	0.2623	0.2618	−1.6	−4.0	−4.2
371.132	16173	A1–B4–C7	0.3262	0.3330	0.3321	−1.6	0.5	0.2
373.115	16173	A2–B5–C8	0.4159	0.4069	0.3936	2.8	0.6	−2.7
375.173	16173	A3–B6–C9	0.4917	0.4872	0.4914	−0.1	−1.1	−0.2
377.138	11590	A1–B4–C7	0.5978	0.6136	0.5997	0.5	3.1	0.8
379.172	11590	A2–B5–C8	0.7542	0.7374	0.7052	4.3	2.0	−2.4
381.178	11590	A3–B6–C9	0.8898	0.8716	0.8601	1.9	−0.2	−1.5

Table 7 Experimental results for the compounds, where *a* and *b* are from Clausius–Clapeyron equation $\ln(p/\mathrm{Pa}) = a - b\,(\mathrm{K}/T)$, and $b = \Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(\langle T\rangle)/R$; $R = 8.314472\ \mathrm{J\ mol^{-1}\ K^{-1}}$

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}	$\Delta_{\mathrm{cr}}^{\mathrm{g}}S_{\mathrm{m}}^{\mathrm{o}}(\langle T\rangle, p\langle T\rangle)$/J mol^{-1} K^{-1}
5-Nitroindazole						
1	35.615	14029.6	388.15	0.589	116.6 ± 1.7	300.5 ± 4.5
2	35.527	14000.3	388.15	0.581	116.4 ± 1.5	299.9 ± 3.8
3	35.702	14072.3	388.15	0.576	117.0 ± 1.7	301.4 ± 4.4
Global	**35.615**	**14034.1**	**388.15**	**0.582**	**116.69 ± 0.94**	**300.6 ± 2.4**
6-Nitroindazole						
1	35.643	13634.2	370.15	0.304	113.4 ± 1.1	306.2 ± 2.9
2	35.738	13672.9	370.15	0.301	113.7 ± 1.0	307.1 ± 2.7
3	35.613	13631.7	370.15	0.297	113.34 ± 0.75	306.2 ± 2.0
Global	**35.646**	**13639.3**	**370.15**	**0.301**	**113.40 ± 0.59**	**306.4 ± 1.6**

Table 8 (p, T) values from the vapour pressure equation

p/Pa:	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
T/K										
5-Nitroindazole	370.1	377.0	381.2	384.2	386.5	388.5	390.1	391.6	392.9	394.1
6-Nitroindazole	359.4	366.1	370.1	373.0	375.3	377.2	378.8	380.3	381.5	382.6

Table 8 lists the (p, T) values calculated from the (p, T) equations for the crystalline compounds, within the experimental pressure range, between 0.1 and 1 Pa.

The standard molar enthalpies of sublimation, at $T = 298.15$ K, were derived from the sublimation enthalpies calculated at the mean temperature $\langle T \rangle$ of the experimental range by Eq. 6:

$$\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^{\mathrm{o}}(T = 298.15\ \mathrm{K}) = \Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^{\mathrm{o}}(\langle T \rangle) + \Delta_{\mathrm{cr}}^{\mathrm{g}} C_{p,\mathrm{m}}^{\mathrm{o}}(298.15\ \mathrm{K} - \langle T \rangle), \tag{6}$$

where $\Delta_{\mathrm{cr}}^{\mathrm{g}} C_{p,\mathrm{m}}^{\mathrm{o}}$ was assumed to be $-50\ \mathrm{J\ K^{-1}\ mol^{-1}}$, in accordance with similar estimations made by Burkinshaw and Mortimer [21], which we have already used in previous papers for other organic compounds [22–39]

Table 9 registers, for each compound, the values of the standard molar enthalpies, entropies and Gibbs energies of sublimation, at $T = 298.15$ K.

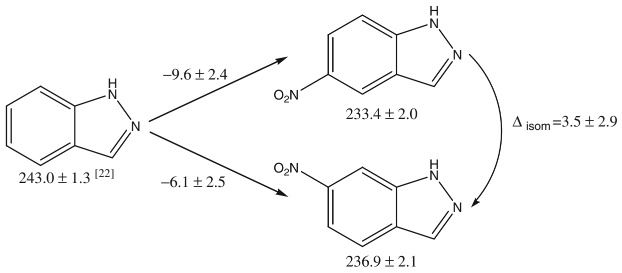
Combining the standard molar enthalpies of formation in the condensed phase with the standard molar enthalpies of sublimation, the standard molar enthalpies of formation in the gas-phase, at $T = 298.15$ K, have been derived, being registered in Table 10.

Discussion

Considering the values of the standard molar enthalpies of formation, in the gaseous phase, of indazole, $\Delta_{\mathrm{f}} H_{\mathrm{m}}^{\mathrm{o}}(\text{indazole, g}) = (243.0 \pm 1.3)\ \mathrm{kJ\ mol^{-1}}$ [40], and the ones derived in this paper for 5- and 6-nitroindazole, the energetic effect due to the introduction of a –NO_2 group in positions 5 and 6 of the indazole ring is derived. As it is shown in Scheme 1, the introduction of the –NO_2 group produces, within the experimental uncertainties, the same effect in both positions, a fact that is also reflected in a low isomerization enthalpy: $\Delta_{\mathrm{isom}} H_{\mathrm{m}}^{\mathrm{o}}(3.5 \pm 2.9)\ \mathrm{kJ\ mol^{-1}}$ (see Scheme 1).

This enthalpic increment is the same that was found for 6-nitroquinoline [30] where the introduction of a –NO_2 group is also, as in the nitroindazoles, an insertion in the benzenic ring of the polycyclic, as shown in Scheme 2.

Comparing the enthalpic increment found for nitroindazoles and nitroquinoline with the one verified in benzene (see also Scheme 2), it is obvious that the introduction of a –NO_2 group in benzene produces a higher stabilizing



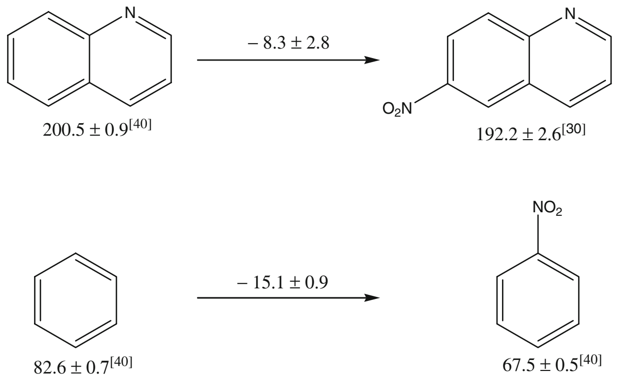
Scheme 1 Enthalpic effect due to the introduction of a nitro group in position 5 and 6 of the indazole. All values in kJ mol^{-1}

Table 9 Derived standard ($p^{\circ} = 0.1$ MPa) molar enthalpies, $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^{\mathrm{o}}$, entropies, $\Delta_{\mathrm{cr}}^{\mathrm{g}} S_{\mathrm{m}}^{\mathrm{o}}$ and Gibbs energies, $\Delta_{\mathrm{cr}}^{\mathrm{g}} G_{\mathrm{m}}^{\mathrm{o}}$, of sublimation, at $T = 298.15$ K

Compound	$\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^{\mathrm{o}}$/kJ mol^{-1}	$\Delta_{\mathrm{cr}}^{\mathrm{g}} S_{\mathrm{m}}^{\mathrm{o}}$/J mol^{-1}K^{-1}	$\Delta_{\mathrm{cr}}^{\mathrm{g}} G_{\mathrm{m}}^{\mathrm{o}}$/kJ mol^{-1}
5-Nitroindazole	121.19 ± 0.94	213.6 ± 2.4	57.5 ± 1.2
6-Nitroindazole	117.00 ± 0.59	211.5 ± 1.6	53.95 ± 0.76

Table 10 Derived Standard ($p^{\circ} = 0.1$ MPa) molar enthalpies of formation, and of phase transition, at $T = 298.15$ K

Compound	$\Delta_{\mathrm{f}} H_{\mathrm{m}}^{\mathrm{o}}$(cr)/ kJ mol^{-1}	$\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^{\mathrm{o}}$/ kJ mol^{-1}	$\Delta_{\mathrm{f}} H_{\mathrm{m}}^{\mathrm{o}}$(g)/ kJ mol^{-1}
5-Nitroindazole	112.2 ± 1.8	121.19 ± 0.94	233.4 ± 2.0
6-Nitroindazole	119.9 ± 2.0	117.00 ± 0.59	236.9 ± 2.1



Scheme 2 Enthalpic effect due to the introduction of a nitro group in position 6 of the quinoline and in benzene. All values in kJ mol^{-1}

effect. As $–NO_2$ is a withdrawing group, the presence of the lone pair in nitrogen atoms of the indazole, or of the quinoline rings, could decrease the electronic delocalization and so, the effect of the $–NO_2$ introduction is not so evident as in benzene.

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