

## Recent work on the thermochemistry of some nitrogen heterocycles

Manuel A. V. Ribeiro da Silva and M. Agostinha R. Matos

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

**Abstract:** Values available in the literature for standard molar enthalpies of formation, both in the condensed and in the gaseous phases, at temperature 298.15 K, for quinolines, methylquinolines, hydroxyquinolines, methylhydroxyquinolines, aminoquinolines, cyanoquinolines, halohydroxyquinolines and nitroquinolines are reviewed, and the results are interpreted in terms of contributions of the different groups and of molecular structure.

### INTRODUCTION

Thermochemical data for chemical compounds are of essential interest for the demands of the ever increasing development of Science and Technology. Such data are important on the understanding of the chemical problems, such as energetics of the chemical bonds, structural properties and reactivity or even in more applied fields like chemical industry, medical and life sciences, military matters, etc.

There is an enormous number of organic compounds of chemical importance, although the number of compounds for which the standard molar enthalpies of formation, both in the condensed and in the gaseous phases, are accurately known with high precision, is very limited. At present, the situation is such that thermochemical data on some classes of compounds, such as hydrocarbons and other aliphatic compounds, are well known and of excellent quality but on other classes, like aromatic and heterocycle compounds, those data are still scarce or even total lacking. Being impossible to measure thermochemical properties for all the known compounds, it is very important to have reliable methods for estimating the enthalpies of formation of different classes of compounds. At the moment, there are several well-established schemes for the estimation of these properties for gaseous aliphatic and alicyclic compounds (ref. 1), but for gaseous aromatic compounds those empirical bond-energy schemes do not apply because they do not account for the effect of perturbations on the  $\pi$ -electron systems. Cox (ref. 2) examined the method of estimating the standard molar enthalpies of formation, in the gaseous state, of substituted benzenes and suggested a scheme based on a constant increment in  $\Delta_f H_m^\circ$  (g) on substitution of a particular group, independent of the position of the substituent, which was later refined by applying correction terms concerning the relative positions on polysubstituted compounds. The estimation of such parameters for heterocycle compounds is even more difficult and problematic since, not only a consistent predicting scheme for these compounds, does not exist, but also because well-established experimental values for key compounds are still scarce.

In order to contribute to the improvement of this situation, during the last few years, we have been performing a systematic thermochemical study on nitrogen heterocycles. In this paper we review the existing literature data for the standard molar enthalpies of formation, both in the condensed and in the gaseous phases, for quinoline derivatives and, whenever possible, try to relate these properties to the sum of contributions from atoms, bonds and groups of atoms, as well as their interactions within the molecule.

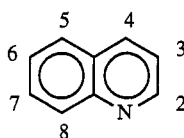
### THERMOCHEMICAL PARAMETERS FOR NITROGEN HETEROCYCLES

The standard molar enthalpies of formation of the compounds, on the condensed phase, were derived from the standard molar energies of combustion, in oxygen, at 298.15 K, measured by static bomb combustion calorimetry (rotating bomb calorimetry was used in the case of halogen derivative compounds), with the amount of substance used in each experiment determined from the total amount of carbon dioxide produced. (ref. 3, 4).

The standard molar enthalpies of sublimation were mainly derived from the vapour pressures as a function of temperature using a mass-loss Knudsen-effusion apparatus (ref. 5). In some cases, the enthalpies of sublimation were measured by the "vacuum sublimation" drop microcalorimetric method (ref. 6).

## QUINOLINE DERIVATIVES

Figure 1 shows the molecular structure of quinoline and the way of numbering the different carbon atoms in order to identify the different derivatives from quinoline.



Literature values for the standard molar enthalpies of formation, in the crystalline and in the gaseous phases, and the standard molar enthalpies of sublimation or vapourization for methyl, hydroxy, hydroxymethyl, amino, cyano, halohydroxy and nitro derivatives of quinoline are resumed in Table 1.

TABLE 1 Standard molar quantities, at 298.15 K (values in  $\text{kJ}\cdot\text{mol}^{-1}$ )

Compound	$\Delta_f H_m^{\circ}(\text{cr,l})$	$\Delta_{\text{cr,l}}^{\text{g}} H_m^{\circ}$	$\Delta_f H_m^{\circ}(\text{g})$	Reference
2-Methylquinoline	$93.0 \pm 2.5$	$66.1 \pm 1.9$	$159.1 \pm 3.1$	7
4-Methylquinoline	$94.5 \pm 2.6$	$67.6 \pm 1.8$	$162.1 \pm 3.2$	7
6-Methylquinoline	$93.3 \pm 2.4$	$67.7 \pm 1.8$	$161.0 \pm 3.0$	7
8-Methylquinoline	$102.0 \pm 2.4$	$65.7 \pm 1.9$	$167.7 \pm 3.1$	7
2,6-Dimethylquinoline	$36.4 \pm 2.5$	$84.5 \pm 1.5$	$120.9 \pm 2.9$	8
2,7-Dimethylquinoline	$34.3 \pm 2.6$	$87.5 \pm 1.5$	$121.8 \pm 3.0$	8
2-Hydroxyquinoline	$-144.9 \pm 2.3$	$119.4 \pm 0.6$	$-25.5 \pm 2.4$	9
4-Hydroxyquinoline	$-114.3 \pm 2.0$	$135.1 \pm 1.1$	$20.8 \pm 2.3$	9
8-Hydroxyquinoline	$-83.0 \pm 1.5$	$89.5 \pm 0.9$	$6.5 \pm 1.7$	10
2-Hydroxy-4-methylquinoline	$-189.1 \pm 2.8$	$128.1 \pm 1.6$	$-61.0 \pm 3.2$	9
4-Hydroxy-2-methylquinoline	$-162.3 \pm 2.7$	$139.0 \pm 1.0$	$-23.3 \pm 2.9$	9
8-Hydroxy-2-methylquinoline	$-129.8 \pm 2.1$	$90.4 \pm 0.7$	$-39.4 \pm 2.2$	10
8-Hydroxy-5-nitroquinoline	$-115.8 \pm 1.7$	$114.1 \pm 2.2$	$-1.7 \pm 2.8$	10
3-Aminoquinoline	$105.3 \pm 2.0$	$103.1 \pm 0.9$	$208.4 \pm 2.2$	11
5-Aminoquinoline	$105.6 \pm 1.9$	$105.0 \pm 0.7$	$210.6 \pm 2.0$	11
6-Aminoquinoline	$100.4 \pm 2.2$	$105.7 \pm 1.0$	$206.1 \pm 2.4$	11
8-Aminoquinoline	$94.3 \pm 2.1$	$93.33 \pm 0.50$	$187.6 \pm 2.2$	11
2-Cyanoquinoline	$246.5 \pm 2.6$	$94.4 \pm 0.7$	$340.9 \pm 2.7$	12
3-Cyanoquinoline	$242.3 \pm 2.0$	$94.2 \pm 0.8$	$336.5 \pm 2.2$	12
5-Chloro-8-hydroxyquinoline	$-124.2 \pm 1.9$	$98.69 \pm 0.86$	$-25.5 \pm 2.1$	13, 14
5,7-Dichloro-8-hydroxyquinoline	$-158.1 \pm 1.8$	$109.3 \pm 0.7$	$-48.8 \pm 1.9$	13, 14
5,7-Dibromo-8-hydroxyquinoline	$-40.5 \pm 2.8$	$117.3 \pm 1.3$	$76.8 \pm 3.1$	13, 14
5,7-Diiodo-8-hydroxyquinoline	$93.5 \pm 1.7$	$126.8 \pm 0.8$	$220.3 \pm 1.9$	13, 14
5-Chloro-7-iodo-8-hydroxyquinoline	—	$114.8 \pm 0.4$	—	13
7-Bromo-5-chloro-8-hydroxyquinoline	$-127.7 \pm 2.1$	$113.2 \pm 0.8$	$-14.5 \pm 2.2$	13, 14
5-Nitroquinoline	$109.2 \pm 2.5$	$94.2 \pm 0.7$	$203.4 \pm 2.6$	15
6-Nitroquinoline	$88.4 \pm 2.2$	$103.8 \pm 1.0$	$192.2 \pm 2.4$	15
8-Nitroquinoline	$100.2 \pm 2.4$	$106.7 \pm 0.9$	$206.9 \pm 2.6$	15

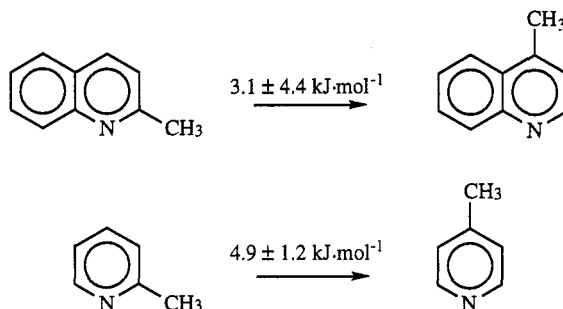
Table 2 contains literature values for the standard molar enthalpies of formation, in the gaseous state, of other compounds which are relevant for the discussion in this paper.

TABLE 2 Standard molar enthalpies of formation of some compounds, in the gaseous state, at 298.15 K

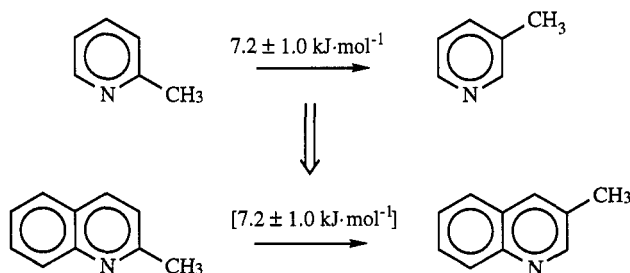
Compound	Formula	$\Delta_f H_m^{\circ}(\text{g}) / \text{kJ}\cdot\text{mol}^{-1}$	Ref.
Pyridine	$\text{C}_5\text{H}_5\text{N}$	$140.4 \pm 0.7$	16
2-Methylpyridine	$2\text{-CH}_3\cdot\text{C}_5\text{H}_4\text{N}$	$99.2 \pm 0.8$	16
3-Methylpyridine	$3\text{-CH}_3\cdot\text{C}_5\text{H}_4\text{N}$	$106.4 \pm 0.6$	16
4-Methylpyridine	$4\text{-CH}_3\cdot\text{C}_5\text{H}_4\text{N}$	$104.1 \pm 0.4$	16
2-Hydroxypyridine	$2\text{-HO}\cdot\text{C}_5\text{H}_4\text{N}$	$-79.7 \pm 1.5$	17
3-Hydroxypyridine	$3\text{-HO}\cdot\text{C}_5\text{H}_4\text{N}$	$-43.7 \pm 1.7$	17
4-Hydroxypyridine	$4\text{-HO}\cdot\text{C}_5\text{H}_4\text{N}$	$-30.3 \pm 5.3$	18
2-Methyl-3-hydroxypyridine	$2\text{-CH}_3\cdot 3\text{-HO}\cdot\text{C}_5\text{H}_3\text{N}$	$-85.8 \pm 1.8$	17
2-Methyl-4-hydroxypyridine	$2\text{-CH}_3\cdot 4\text{-HO}\cdot\text{C}_5\text{H}_3\text{N}$	$-71.7 \pm 1.7$	17
2-Methyl-6-hydroxypyridine	$2\text{-CH}_3\cdot 4\text{-HO}\cdot\text{C}_5\text{H}_3\text{N}$	$-120.3 \pm 2.5$	17
Quinoline	$\text{C}_9\text{H}_7\text{N}$	$200.54 \pm 0.94$	19
Benzene	$\text{C}_6\text{H}_6$	$82.6 \pm 0.7$	16
Toluene	$\text{C}_6\text{H}_5\text{CH}_3$	$50.4 \pm 0.6$	16

### Methylquinolines

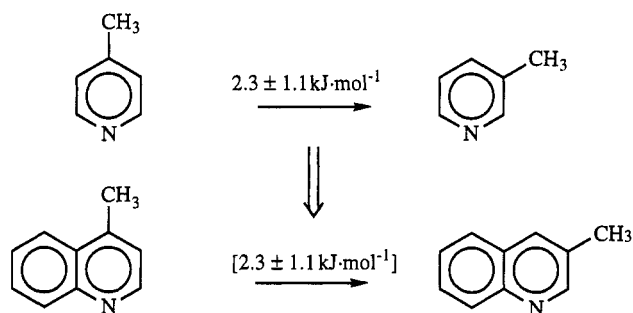
For methylquinolines and methylpyridines the enthalpies of isomerization in the gaseous state, of the methyl group from the *ortho* to the *para* position, relative to the pyridinic nitrogen, are the same within the experimental uncertainties associated:



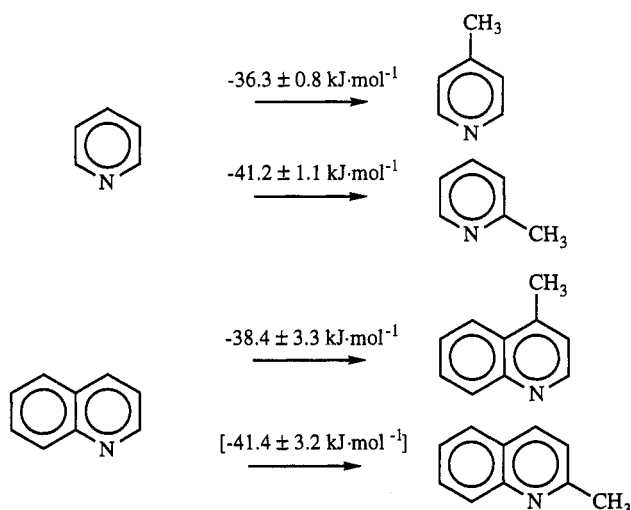
Thus, if we assume that the isomerization of the *ortho* methyl group to the *meta* position in pyridines ( $7.2 \pm 1.0$ )  $\text{kJ}\cdot\text{mol}^{-1}$ , is enthalpically similar in quinolines, a value of  $(166.3 \pm 3.2)$   $\text{kJ}\cdot\text{mol}^{-1}$  can be estimated for the standard molar enthalpy of formation of 3-methylquinoline.



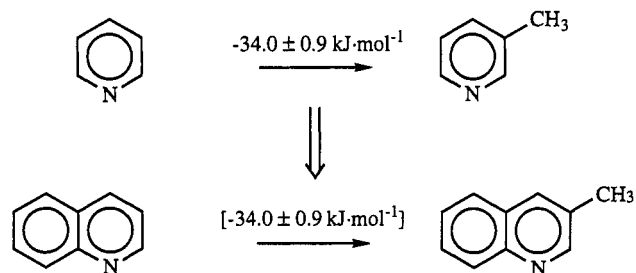
In a similar way, using the enthalpic increment for the *para* to *meta* isomerization, in the gaseous state, in methylpyridines,  $(2.3 \pm 1.1)$   $\text{kJ}\cdot\text{mol}^{-1}$ , and  $\Delta_f H_m^{\circ}$ (4-methylquinoline, g) it can be estimated the value  $\Delta_f H_m^{\circ}$ (3-methylquinoline, g) =  $(164.5 \pm 3.7)$   $\text{kJ}\cdot\text{mol}^{-1}$ .



From literature values for methylpyridines (Table 2) and of  $\Delta_f H_m^\circ$ (methylquinoline, g) it is clear that the enthalpy increments for methyl substitution into the pyridine ring of quinoline in *ortho* or *para* positions are the same as those in pyridine:

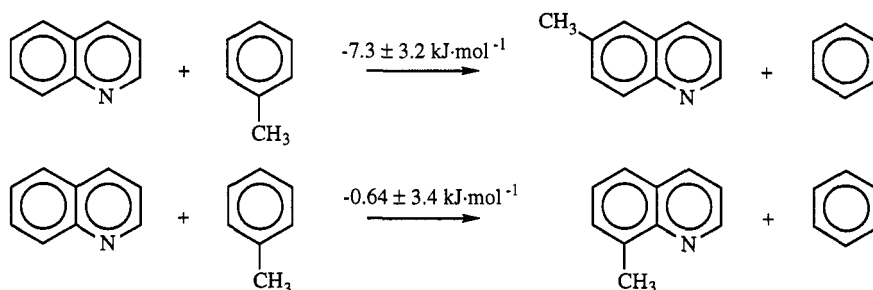


Thus it is reasonable to expect that the same would happen for the insertion of a methyl group in the *meta* position of both pyridine and quinoline, and so to estimate  $\Delta_f H_m^\circ$ (3-methylquinoline, g) =  $(166.5 \pm 1.3) \text{ kJ}\cdot\text{mol}^{-1}$ , using the values of  $\Delta_f H_m^\circ$ (g) for quinoline, pyridine and 3-methylpyridine.



The three estimated values for  $\Delta_f H_m^\circ$ (3-methylquinoline, g) are in perfect agreement so it can be assumed that the standard molar enthalpy of formation of gaseous 3-methylquinoline is the weighted mean (ref. 20) of these values:  $(166.4 \pm 1.1) \text{ kJ}\cdot\text{mol}^{-1}$ .

Since the hypothetical gaseous redistribution reactions:



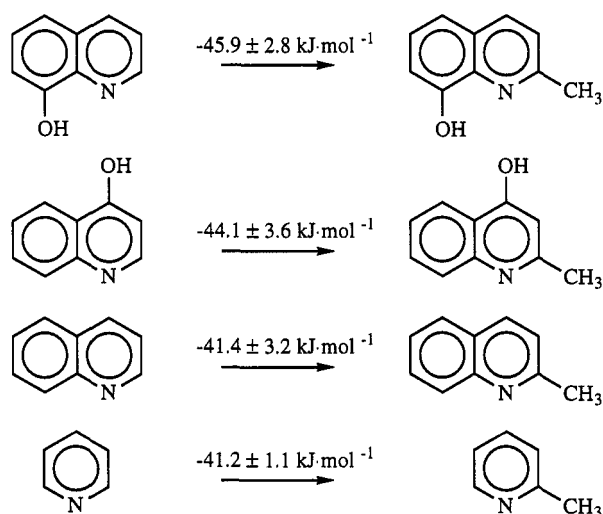
are almost thermoneutral, [ $\Delta_f H_m^\circ = -(7.3 \pm 3.2) \text{ kJ}\cdot\text{mol}^{-1}$  and  $-(0.64 \pm 3.4) \text{ kJ}\cdot\text{mol}^{-1}$ , respectively], it can be concluded that the enthalpic increment for the methyl substitution into the benzenic ring of quinoline is the same as that in benzene, so it would be expected that the values for  $\Delta_f H_m^\circ$  of 5-methylquinoline (g) and of 7-methylquinoline (g) would be very similar, *i.e.*  $(168.3 \pm 1.3) \text{ kJ}\cdot\text{mol}^{-1}$ .

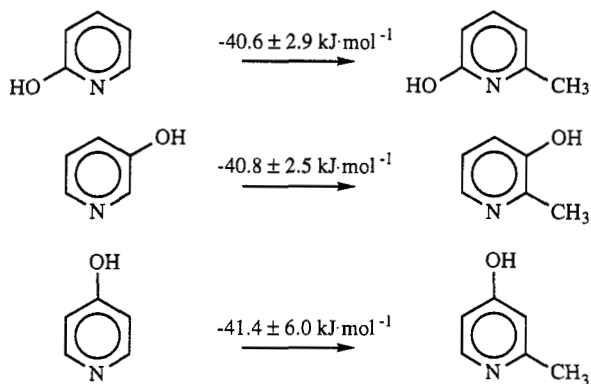
The standard molar enthalpies of formation of both 2,6- and 2,7-dimethylquinoline in the gaseous state can now be estimated from the standard molar enthalpy of the gaseous quinoline by adding the values for the increments in enthalpy of formation for methyl substitution into benzene:  $-(32.2 \pm 1.0) \text{ kJ}\cdot\text{mol}^{-1}$ , and for methyl substitution into the *ortho* position in pyridine:  $-(41.2 \pm 1.1) \text{ kJ}\cdot\text{mol}^{-1}$ , to yield, for both isomers, an estimated  $\Delta_f H_m^\circ(\text{g}) = (127.1 \pm 1.8) \text{ kJ}\cdot\text{mol}^{-1}$ . These estimates are within  $10 \text{ kJ}\cdot\text{mol}^{-1}$  of the experimental values, which constitutes satisfactory agreement for such a method of estimation.

### Hydroxyquinolines and hydroxymethylquinolines

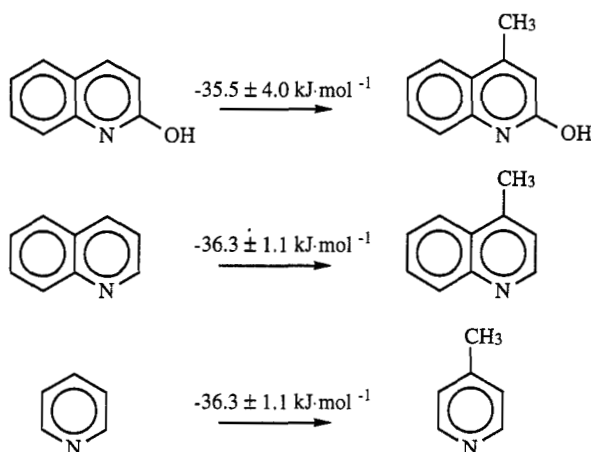
To establish some conclusions concerning the enthalpic effect of the position of substitution of methyl and hydroxyl groups on of these heterocyclic molecules, the experimental values on Table 1 should be considered together with those in Table 2 for some gaseous methylpyridines and hydroxypyridines.

The following scheme presents a comparative study of the effect due to the introduction of a methyl group in an *ortho* position relative to the nitrogen heteroatom on the values of the standard molar enthalpies of formation. This substitution for the hydroxyquinolines leads to an increment  $\Delta\{\Delta_f H_m^\circ(\text{g})\}$  of about  $-(45 \pm 4) \text{ kJ}\cdot\text{mol}^{-1}$ . Similar introduction in the *ortho* position in quinoline, pyridine and hydroxypyridines, leads to a constant increment of about  $-(41 \pm 4) \text{ kJ}\cdot\text{mol}^{-1}$ . These increments are equal within the associated uncertainties.



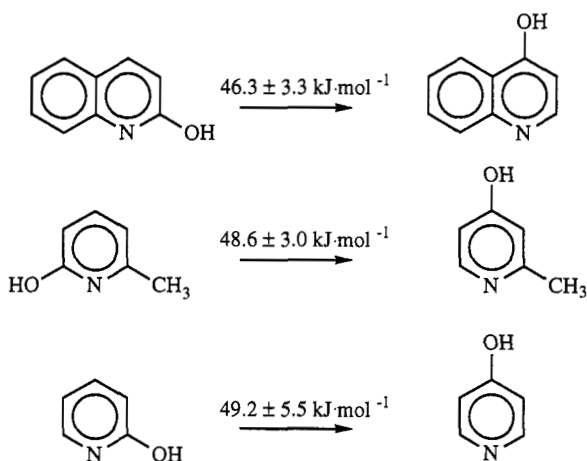


The following scheme shows that the increment for the introduction of a methyl group in the *para* position relative to the nitrogen, is, within the associated uncertainties, apparently the same for pyridine, quinoline and hydroxyquinoline, and of about  $-36 \text{ kJ}\cdot\text{mol}^{-1}$ .

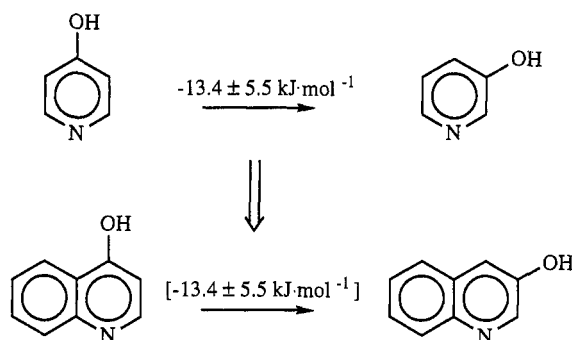


The effect of the addition of a methyl group to the pyridinic ring of hydroxyquinolines depends, mainly, on its relative position to the heteroatom, rather than its relative position to the hydroxyl group. The same effect is verified in the addition of a methyl group to the hydroxypyridines.

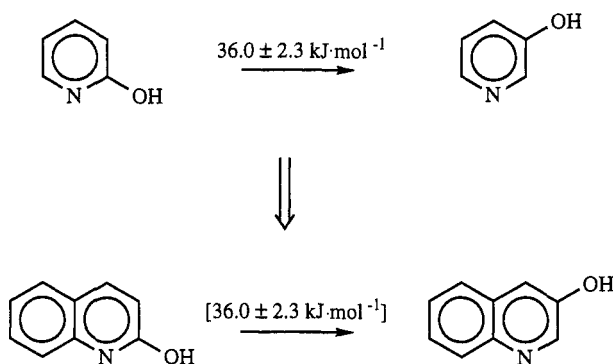
The enthalpies of isomerization of the *ortho* hydroxy group to the *para* position relative to the nitrogen are, within the associated uncertainties, the same in hydroxyquinolines and in pyridines, as can be seen from the following scheme.



It is reasonable to assume that the enthalpies of isomerisation of the *para* hydroxy group to the *meta* position have similar values for hydroxypyridines and hydroxyquinolines which permits the estimation of a value for the molar enthalpy of formation of 3-hydroxyquinoline as  $(7.4 \pm 6.0) \text{ kJ}\cdot\text{mol}^{-1}$ .

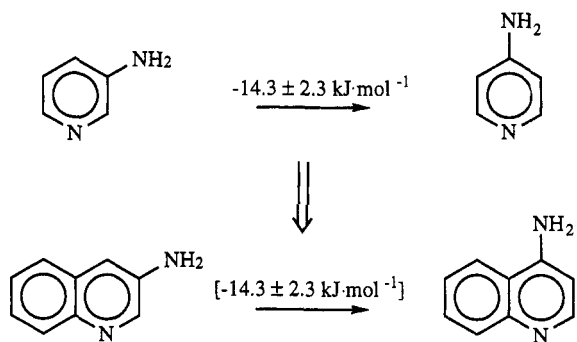


The predicted enthalpy of formation  $(7.4 \pm 6.0) \text{ kJ}\cdot\text{mol}^{-1}$  is equal to the value  $(10.5 \pm 3.3) \text{ kJ}\cdot\text{mol}^{-1}$  derived, by assuming the same value of  $\Delta_{\text{isom}} H_{\text{m}}^{\circ}$ , for the *ortho*-hydroxy group to the *meta* position, both in pyridine and quinoline:



### Aminoquinolines

In similar fashion, from the enthalpies of isomerisation of the *meta*-amino group in pyridine to the *para* and to the *ortho* positions, assuming that their respective values are equal to those for the corresponding isomerisations in quinoline, estimations were made for the enthalpies of formation of 4-aminoquinoline  $(194.1 \pm 3.2) \text{ kJ}\cdot\text{mol}^{-1}$  and of 2-aminoquinoline  $(182.3 \pm 2.9) \text{ kJ}\cdot\text{mol}^{-1}$ . Values for the standard molar enthalpies of formation of the aminopyridines, in the gaseous state, used on the following calculations, are registered in Table 3.



$$\Delta_{\text{f}} H_{\text{m}}^{\circ} = [194.1 \pm 3.2 \text{ kJ}\cdot\text{mol}^{-1}]$$

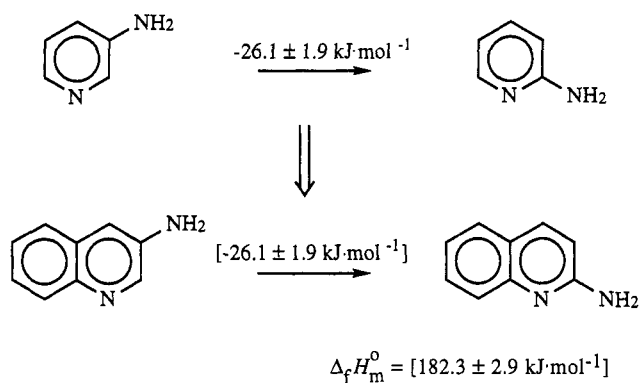
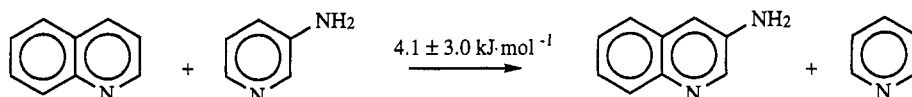


TABLE 3. Standard molar enthalpies of formation of aminopyridines, in the gaseous state, at 298.15 K.(ref. 21)

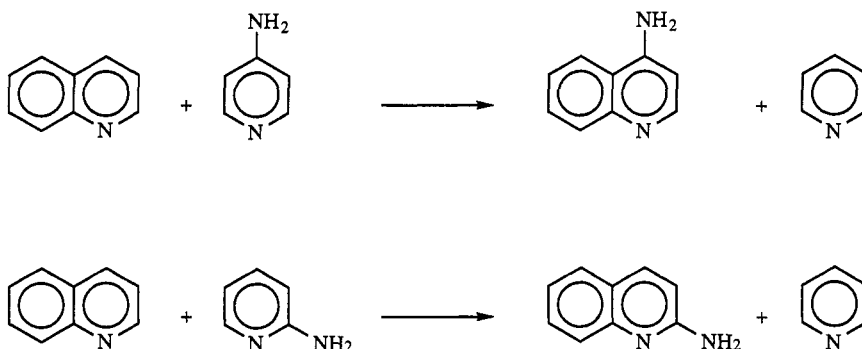
Compound	$\Delta_f H_m^0(\text{g}) / \text{kJ}\cdot\text{mol}^{-1}$
2-Aminopyridine	$118.1 \pm 1.1$
3-Aminopyridine	$144.2 \pm 1.6$
4-Aminopyridine	$129.9 \pm 1.4$

Since the hypothetical gaseous redistribution reaction:



is nearly thermoneutral ( $4.1 \pm 3.0$ )  $\text{kJ}\cdot\text{mol}^{-1}$ , we conclude that the enthalpy increment for amino substitution in the pyridinic ring of quinoline is the same as that in pyridine.

Because both 2-, and 4-aminoquinoline are describable using similar redistribution reactions (which are assumed to be thermoneutral)



values can be derived for the enthalpies of formation of these isomers from the enthalpies of formation of quinoline, pyridine, and of 2-, or 4-aminopyridine, respectively.

The estimated values,  $(178.2 \pm 1.6)$   $\text{kJ}\cdot\text{mol}^{-1}$  and  $(190.0 \pm 1.8)$   $\text{kJ}\cdot\text{mol}^{-1}$ , respectively for 2-aminoquinoline and 4-aminoquinoline are in agreement with those predicted from the isomerisation reactions as above. Following this procedure, one can estimate for standard molar enthalpies of formation, at 298.15 K, in the gaseous state, of 2- and 4-aminoquinoline, the weighted mean values derived by the previous procedures, as  $\Delta_f H_m^0(2\text{-aminoquinoline}) = (179.2 \pm 1.4)$   $\text{kJ}\cdot\text{mol}^{-1}$  and  $\Delta_f H_m^0(4\text{-aminoquinoline}) = (191.0 \pm 1.6)$   $\text{kJ}\cdot\text{mol}^{-1}$ .



To estimate the enthalpies of formation in the gaseous state of quinoline derivatives with substituents in the benzenic ring, it would seem appropriate to apply the Cox scheme (ref. 2), developed for substituted benzenes, in which transferability of bond enthalpy contributions with corrections + 4 kJ·mol<sup>-1</sup> for each pair of *ortho* substituents and an additional correction of + 4 kJ·mol<sup>-1</sup> for each set of substituents, in position 1,2,3, could be used to estimate  $\Delta_f H_m^\circ$ , for substituted benzenes, within  $\pm 10$  kJ·mol<sup>-1</sup>. With  $\Delta_f H_m^\circ$ , (aniline, g) = (87.1  $\pm$  1.0) kJ·mol<sup>-1</sup> (ref. 16) the estimated values for 5- and 6- aminoquinolines are (204.7  $\pm$  10.0) kJ·mol<sup>-1</sup> differing only by 5.9 and 1.4 kJ·mol<sup>-1</sup> from the experimental results. Such estimations however, would not be sensible for substitution into the 8-position because of interaction with the pyridinic nitrogen atom.

### Cyanoquinolines

Table 4 summarizes the available experimental values of the standard molar enthalpies of formation in the gaseous state of cyanopyridines and cyanoquinolines, as well as the enthalpic increments for the CN-substitutions into pyridine and quinoline. It is clear from the table that the enthalpic increments of cyano substituents into the heterocycle rings of pyridine and quinoline are, within the experimental uncertainties ascribed to them, very similar, depending only on the position where the substitution takes place. Thus, it seems reasonable to estimate, the standard molar enthalpy of formation, in the gaseous phase, of 4-cyanoquinoline, assuming the same increment as the one for cyano-substitution into position 4 of pyridine which yields  $\Delta_f H_m^\circ$ (4-CN-C<sub>9</sub>H<sub>6</sub>N, g) = (343.6  $\pm$  1.6) kJ·mol<sup>-1</sup>.

TABLE 4. Experimental standard molar enthalpies of formation, in the gaseous state, at 298.15 K and enthalpic increments for CN-substitution into pyridine (Py), C<sub>5</sub>H<sub>5</sub>N, and quinoline (Q), C<sub>9</sub>H<sub>7</sub>N. Values in kJ·mol<sup>-1</sup>

Compound	$\Delta_f H_m^\circ$ (g)	$\Delta[\Delta_f H_m^\circ$ (g)]		Compound	$\Delta_f H_m^\circ$ (g)	$\Delta[\Delta_f H_m^\circ$ (g)]
		Py	→ CN-Py			
C <sub>5</sub> H <sub>5</sub> N	140.4 $\pm$ 0.7 <sup>16</sup>	–	–	C <sub>9</sub> H <sub>7</sub> N	200.54 $\pm$ 0.94 <sup>19</sup>	–
2-CN-C <sub>5</sub> H <sub>4</sub> N	280.7 $\pm$ 1.5 <sup>22</sup>	140.3 $\pm$ 1.7	–	2-CN-C <sub>9</sub> H <sub>6</sub> N	340.9 $\pm$ 2.7 <sup>12</sup>	140.4 $\pm$ 2.8
3-CN-C <sub>5</sub> H <sub>4</sub> N	277.9 $\pm$ 2.0 <sup>22</sup>	137.5 $\pm$ 2.1	–	3-CN-C <sub>9</sub> H <sub>6</sub> N	336.5 $\pm$ 2.2 <sup>12</sup>	136.0 $\pm$ 2.4
4-CN-C <sub>5</sub> H <sub>4</sub> N	283.5 $\pm$ 1.1 <sup>22</sup>	143.1 $\pm$ 1.3	–	–	–	–

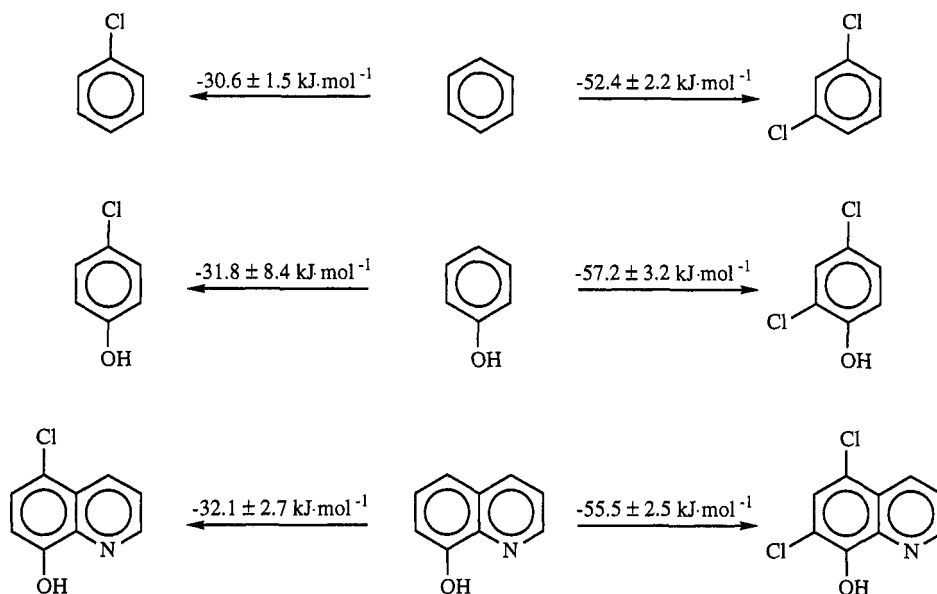
### Halohydroxyquinolines

The lack of literature values for bromophenols and iodophenols limits the discussion to chlorophenols and suggests that the standard molar enthalpies of formation of bromo- and iodophenols should be measured in order to assess the validity of this additive scheme.

With the auxiliary data of Tables 2 and 5, it is clear that the enthalpic increments for substitution of chlorine atoms, in equivalent positions, into benzene, phenol and 8-hydroxyquinoline are virtually the same.

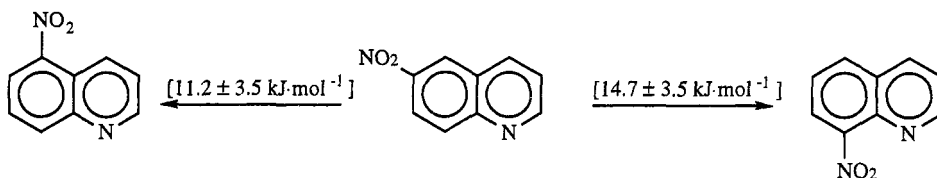
TABLE 5. Standard molar enthalpies of formation, in the gaseous state, at 298.15 K

Compound	Formula	$\Delta_f H_m^\circ$ (g) / kJ·mol <sup>-1</sup>	Ref.
Chlorobenzene	C <sub>6</sub> H <sub>5</sub> Cl	52.0 $\pm$ 1.3	16
1,3-Dichlorobenzene	C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	30.2 $\pm$ 2.1	16
Phenol	C <sub>6</sub> H <sub>5</sub> OH	– 96.4 $\pm$ 0.9	16
4-Chlorophenol	C <sub>6</sub> H <sub>4</sub> ClOH	– 128.2 $\pm$ 8.6	23, 24
2,4-Dichlorophenol	C <sub>6</sub> H <sub>3</sub> Cl <sub>2</sub> OH	– 153.6 $\pm$ 1.9	23



### Nitroquinolines

Considering the enthalpies of isomerization below, to show that 6-nitroquinoline, the most stable of the



isomers is essentially relatively strain-free, then 5-nitroquinoline is strained relatively to the 6 isomer by  $(11.2 \pm 3.5) \text{ kJ}\cdot\text{mol}^{-1}$ , presumably because the hydrogen atom in the 4 position is closer to the nitro group than the 5 and 7 hydrogen atoms to the nitro group in the 6 position. The 8-nitroquinoline is relatively more strained by  $(14.7 \pm 3.5) \text{ kJ}\cdot\text{mol}^{-1}$ , because of repulsion between the oxygen atom of the nitro group and the quinoline nitrogen atom.

The increments for substitution of a methyl group into the 2 position is for 8-nitroquinoline  $-(40.5 \pm 3.6) \text{ kJ}\cdot\text{mol}^{-1}$ , for quinoline  $-(41.4 \pm 3.2) \text{ kJ}\cdot\text{mol}^{-1}$ , for 8-hydroxyquinoline  $-(45.9 \pm 2.8) \text{ kJ}\cdot\text{mol}^{-1}$  and for pyridine  $-(41.2 \pm 1.1) \text{ kJ}\cdot\text{mol}^{-1}$ . These increments all agree among themselves within the limits of experimental uncertainty thus permitting the reliable estimation of the enthalpies of formation of other isomers in the gaseous state.

### **Acknowledgements**

Thanks are due to JNICT, Junta Nacional de Investigação Científica e Tecnológica, Lisbon, Portugal for financial support given to the Thermochemistry Research Group of the Chemistry Research Center of the University of Oporto. One of us (M.A.V.R.S.) also thanks Fundação Calouste Gulbenkian, Lisbon, Portugal, for the awarding of a travel grant which made possible to give this invited lecture at the 14th International Conference on Chemical Thermodynamics, in Osaka, Japan.

## REFERENCES

1. J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*, Academic Press: London and New York. (1970).
2. J. D. Cox *A Method for Estimating the Enthalpies of Formation of Benzene Derivatives in the Gas State*. NPL Report CHEM 83, June 1978.
3. M. D. M. C. Ribeiro da Silva, M. A. V. Ribeiro da Silva and G. Pilcher, *J. Chem. Thermodynamics*, **16**, 1149 (1984).
4. M. A. V. Ribeiro da Silva, M. D. M. C. Ribeiro da Silva and G. Pilcher, *Rev. Port. Quim.* **26**, 163 (1984).
5. M. A. V. Ribeiro da Silva and M. J. S. Monte, *Thermochim. Acta*, **171**, 169 (1990).
6. F. A. Adedji, D. L. S. Brown, J. A. Connor, M. Leung, M. I. Paz Andrade and H. A. Skinner, *J. Organometallic Chem.*, **97**, 221 (1975).
7. M. A. V. Ribeiro da Silva, M. A. R. Matos and L. M. P. F. Amaral, *J. Chem. Thermodynamics*, **27**, 565 (1995).
8. M. A. V. Ribeiro da Silva, M. A. R. Matos and L. M. P. F. Amaral, *J. Chem. Thermodynamics*, **27**, 1141 (1995).
9. M. A. V. Ribeiro da Silva, M. A. R. Matos and M. J. S. Monte, *J. Chem. Thermodynamics*, **22**, 609 (1990).
10. M. A. V. Ribeiro da Silva, M. J. S. Monte and M. A. R. Matos *J. Chem. Thermodynamics*, **21**, 159 (1989).
11. M. A. V. Ribeiro da Silva, M. A. R. Matos and L. M. P. F. Amaral, *J. Chem. Thermodynamics*, **27**, 1187 (1995).
12. M. A. V. Ribeiro da Silva, M. A. R. Matos, M. J. S. Monte, M. C. B. Alves and J. M. A. P. Vieira, *J. Chem. Thermodynamics*, **25**, 579 (1993).
13. M. A. V. Ribeiro da Silva and M. J. S. Monte, *J. Chem. Thermodynamics*, **24**, 715 (1992).
14. M. A. V. Ribeiro da Silva, M. L. C. C. H. Ferrão and A. M. R. O. Alves da Silva, *J. Chem. Thermodynamics*, **27**, 633 (1995).
15. M. A. V. Ribeiro da Silva, M. A. R. Matos and L. M. P. F. Amaral, *J. Chem. Thermodynamics*, in press (1996).
16. J. B. Pedley, *Thermochemical Data and Structures of Organic Compounds, Vol. I*, Thermodynamics Research Center, College Station, Texas, USA, (1994).
17. S. Suradi, N. El Saiad, G. Pilcher and H. A. Skinner, *J. Chem. Thermodynamics*, **14**, 45 (1982).
18. M. A. V. Ribeiro da Silva, M. A. R. Matos, Y. Meng-Yan and G. Pilcher, *J. Chem. Thermodynamics*, **24**, 107 (1992).
19. W. V. Steele, D. V. Archer, R. D. Chirico, W. B. Collier, I. A. Hossenlopp, A. Nguren, N. K. Smith and B. E. Gammon, *J. Chem. Thermodynamics*, **20**, 1233 (1988).
20. G. Olofsson, *Experimental Chemical Thermodynamics, Vol. I - Combustion Calorimetry*, S. Sunner and M. Mansson: editors. Pergamon Press: Oxford, (1979).
21. J. Bickerton and G. Pilcher, *J. Chem. Thermodynamics*, **16**, 373 (1984).
22. J. Bickerton, G. Pilcher and G. Al-Takhin, *J. Chem. Thermodynamics*, **16**, 378 (1984).
23. M. A. V. Ribeiro da Silva, M. L. C. C. H. Ferrão and F. Jiye, *J. Chem. Thermodynamics*, **26**, 839 (1994).
24. L. Smith, L. Bjellerup, S. Kroops and H. Westermarck, *Acta Chem. Scand.*, **7**, 65 (1953).