

# Thermochemical study of cyanopyrazines: Experimental and theoretical approaches

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## Abstract

The standard ( $p^\circ = 0.1$  MPa) molar energy of combustion, at  $T = 298.15$  K, of crystalline 2,3-dicyanopyrazine was measured by static bomb calorimetry, in oxygen atmosphere. The standard molar enthalpy of sublimation, at  $T = 298.15$  K, was obtained by Calvet Microcalorimetry, allowing the calculation of the standard molar enthalpy of formation of the compound, in the gas phase, at  $T = 298.15$  K:  $\Delta_f H_m^\circ(g) = (518.7 \pm 3.4) \text{ kJ} \cdot \text{mol}^{-1}$ .

In addition, the geometries of all cyanopyrazines were obtained using density functional theory with the B3LYP functional and two basis sets: 6-31G\* and 6-311G\*\*. These calculations were then used for a better understanding of the relation between structure and energetics of the cyanopyrazine systems. These calculations also reproduce measured standard molar enthalpies of formation with some accuracy and do provide estimates of this thermochemical parameter for those compounds that could not be studied experimentally, namely the tri- and tetracyanopyrazines: the strong electron withdrawing cyano group on the pyrazine ring makes cyanopyrazines highly destabilized compounds.

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**Keywords:** Cyanopyrazines; Energy of combustion; Enthalpy of sublimation; Enthalpy of formation; Theoretical calculations

## 1. Introduction

The thermochemical study of pyrazine derivatives has been a continuing interest of researchers in our laboratory, in order to establish relationships among the structural and energetical properties in this kind of compounds [1–7]. It is our aim with this paper to enlarge the thermochemical database as well as to predict theoretically thermochemical parameters for other compounds whose experimental study is impossible due to difficulties in their synthesis and/or in obtaining them pure in the needed quantity.

We have performed the experimental study of cyanopyrazine [7] and in the present work we report the standard molar enthalpy of formation of 2,3-dicyanopyrazine (2,3-DCNPz) in the gaseous phase, obtained from measurements of the combustion energy using a static bomb calorimeter and from the enthalpy of sublimation of the compound measured by microcalorimetry Calvet. Experimental determinations for tri- and tetracyanopyrazine were precluded due to the impossibility to obtain pure samples of the compounds in the needed quantity. So, we have decided to perform theoretical calculations as a complement to the experimental work. Density functional theory (DFT) calculations were performed in order to obtain the optimized geometry of 2,3-dicyanopyrazine and of all the other possible isomers, as well as, all the other cyanopyrazines. Estimates of the

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enthalpies of formation for all the cyanopyrazines were thus obtained from the DFT calculations.

The 2,3-dicyanopyrazine derivatives are very powerful electron acceptors and valuable in a broad range of chemistry fields for their application to dyestuff and nonlinear optical materials [8]. Compounds containing the 2,3-dicyanopyrazine unit are especially suitable building blocks for the strong intramolecular charge-transfer chromophoric system which is necessary for second order nonlinear optical materials [9]. The 2,3-dicyano-5-methylpyrazines can be used as convenient precursors for fluorescent dyes, and can be applied jointly with other compounds as emitters for electroluminescence devices [9].

## 2. Experimental

### 2.1. Materials

The 2,3-DCNPz obtained commercially from Aldrich Chemical Co. [13481-25-9], with the minimum mass fraction of purity of 0.99, was further purified by repeated sublimation under reduced pressure until the combustion results were consistent and the carbon dioxide recovery ratios were satisfactory. The average ratio, together with the standard deviation of the mean, of the mass of carbon dioxide recovered to that calculated from the mass of sample was  $(0.9999 \pm 0.0001)$ . The final purity of the compound was further assessed by differential scanning calorimetry (DSC) using the fractional fusion technique [10]. The mass fraction of impurities found was less than  $1 \times 10^{-3}$ . The temperature and the enthalpy of fusion of the purified samples (hermetically sealed in steel crucibles) were measured using a Setaram DSC 141 apparatus under a heating rate of  $3.3 \times 10^{-2} \text{ K} \cdot \text{s}^{-1}$ . The power scale of the calorimeter was calibrated with high-purity indium (mass fraction  $> 0.99999$ ) and its temperature scale was calibrated by measuring the melting temperature of the following high purity reference materials [11]: naphthalene, benzoic acid and indium. The recorded thermograms do not show any phase transitions between  $T = 298 \text{ K}$  and the melting temperature of the samples. The temperature of fusion (observed at the onset of the calorimetric peaks),  $T_{\text{fus}}$ , and the molar enthalpy of fusion were computed from the DSC thermograms,  $\Delta_{\text{cr}}^{\text{f}} H_{\text{m}} (T_{\text{fus}} = (405.06 \pm 0.05 \text{ K})) = (19.80 \pm 0.31) \text{ kJ} \cdot \text{mol}^{-1}$ . The uncertainties assigned to the last values are twice the standard deviation of the mean of five independent runs. The density for 2,3-DCNPz was estimated as  $\rho = 1.13 \text{ g} \cdot \text{cm}^{-3}$  at  $T = 298 \text{ K}$ .

### 2.2. Combustion calorimetry

The combustion experiments were performed with a static bomb calorimeter. The apparatus and technique

have been described previously [12,13]. Benzoic acid (Bureau of Analysed Samples, Thermochemical Standard, BCS-CRM-190r) was used for calibration of the bomb. Its massic energy of combustion is  $\Delta_{\text{c}} u = -(26432.3 \pm 3.8) \text{ J} \cdot \text{g}^{-1}$ , under certificate conditions. The calibration results were corrected to give the energy equivalent  $\varepsilon_{\text{cal}}$  corresponding to the average mass of water added to the calorimeter: 3119.6 g. From six calibration experiments,  $\varepsilon_{\text{cal}} = (16007.3 \pm 0.7) \text{ J} \cdot \text{K}^{-1}$ , where the uncertainty quoted is the standard deviation of the mean. The 2,3-DCNPz was burnt, in pellet form, in oxygen at the pressure 3.04 MPa with  $1.00 \text{ cm}^3$  of water added to the bomb. For all experiments, ignition was made at  $T = (298.150 \pm 0.001) \text{ K}$ . The electrical energy for ignition was determined from the change in potential difference across a capacitor when discharged through the platinum ignition wire. For the cotton-thread fuse, empirical formula  $\text{CH}_{1.686}\text{O}_{0.843}$ , the standard massic energy of combustion is  $\Delta_{\text{c}} u^{\circ} = -16250 \text{ J} \cdot \text{g}^{-1}$  [14]. This value has been confirmed by previous combustion of cotton-thread samples in our laboratory. The corrections for nitric acid formation were based on  $-59.7 \text{ kJ} \cdot \text{mol}^{-1}$  [15], for the molar energy of formation of  $0.1 \text{ mol} \cdot \text{dm}^{-3} \text{ HNO}_3(\text{aq})$  from  $\text{N}_2(\text{g})$ ,  $\text{O}_2(\text{g})$ , and  $\text{H}_2\text{O}(\text{l})$ . The amount of substance used in each experiment was determined from the total mass of carbon dioxide produced after allowance for that formed from the cotton thread fuse. An estimated pressure coefficient of massic energy:  $(\partial u / \partial p)_T = -0.2 \text{ J} \cdot \text{g}^{-1} \cdot \text{MPa}^{-1}$  at  $T = 298.15 \text{ K}$ , a typical value for most organic compounds [16], was assumed. The standard massic energy of combustion,  $\Delta_{\text{c}} u^{\circ}$ , for 2,3-DCNPz was calculated using the procedure given by Hubbard *et al.* [17]. The molar masses used for the elements were those recommended by the IUPAC commission [18].

### 2.3. Microcalorimetry Calvet

The standard molar enthalpy of sublimation of 2,3-DCNPz was measured using the “vacuum sublimation” drop microcalorimetric method [19]. Samples, about 3 mg of the crystalline compound, contained in thin glass capillary tubes sealed at one end, were dropped, at room temperature, into the hot reaction vessel, in the Calvet high temperature microcalorimeter (SETARAM HT 1000) held at a convenient temperature of 385 K, and then removed from the hot zone by vacuum sublimation. Simultaneously, an empty capillary tube was dropped in the reference calorimetric cell. The observed standard molar enthalpy of sublimation  $\Delta_{\text{cr},298.15 \text{ K}}^{\text{gT}} H_{\text{m}}^{\circ}$  was corrected to  $T = 298.15 \text{ K}$  using the value of  $\Delta_{298.15 \text{ K}}^{\text{gT}} H_{\text{m}}^{\circ}(\text{g})$  estimated by a group method with values from Stull *et al.* [20]. The microcalorimeter was calibrated *in situ* for these measurements using the reported standard molar enthalpy of sublimation of naphthalene [21].

TABLE 1  
Combustion experiment results, at  $T = 298.15$  K

$m(\text{CO}_2, \text{total})/\text{g}$	1.00475	1.56491	1.88848	1.69284	1.92239	1.95646
$m(\text{cpd})/\text{g}$	0.49304	0.76865	0.92820	0.83183	0.94482	0.96185
$m(\text{fuse})/\text{g}$	0.00266	0.00304	0.00289	0.00285	0.00300	0.00269
$\Delta T_{\text{ad}}/\text{K}$	0.73561	1.14485	1.38208	1.23742	1.40496	1.43221
$\varepsilon_f/(\text{J} \cdot \text{K}^{-1})$	14.79	14.85	14.97	14.87	15.00	14.98
$\Delta m(\text{H}_2\text{O})/\text{g}$	0.0	0.0	0.0	0.0	−0.1	0.0
$-\Delta U(\text{IBP})/\text{J}$	11784.81	18341.77	22142.86	19824.95	22508.90	22946.08
$-\Delta U(\text{HNO}_3)/\text{J}$	47.70	74.03	87.76	82.68	86.92	92.24
$-\Delta U(\text{carbon})/\text{J}$	0.00	0.00	0.00	0.00	0.00	0.00
$\Delta U(\text{ign.})/\text{J}$	1.20	1.19	1.20	1.20	1.20	1.19
$-\Delta U_{\Sigma}/\text{J}$	12.73	20.08	24.46	21.72	24.98	25.36
$-\Delta U(\text{fuse})/\text{J}$	43.20	49.37	46.93	46.28	48.72	43.69
$-\Delta_c u^\circ/(\text{J} \cdot \text{g}^{-1})$	23692.15	23675.65	23684.24	23651.79	23653.48	23688.51
$\Delta_c u^\circ = -(23674.3 \pm 7.2) \text{ J} \cdot \text{g}^{-1}$						

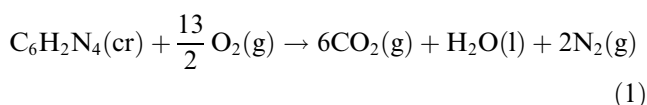
$m(\text{CO}_2, \text{total})$  is the total mass of  $\text{CO}_2$  formed in the experiment;  $m(\text{cpd})$  is the mass of compound burnt in the experiment;  $m'(\text{fuse})$  is the mass of fuse (cotton) used in the experiment;  $\Delta T_{\text{ad}}$  is the corrected temperature rise;  $\varepsilon_f$  is the energy equivalent of contents in the final state;  $\Delta m(\text{H}_2\text{O})$  is the deviation of the mass of water added to the calorimeter from 3119.6 g;  $\Delta U(\text{IBP})$  is the energy change for the isothermal combustion reaction under actual bomb conditions;  $\Delta U(\text{IBP})$  includes  $\Delta U(\text{ign.})$ ;  $\Delta U(\text{HNO}_3)$  is the energy correction for the nitric acid formation;  $\Delta U(\text{carbon})$  is the energy correction for carbon formation;  $\Delta U(\text{ign.})$  is the energy of combustion of the fuse;  $\Delta U_{\Sigma}$  is the energy correction to the standard state;  $\Delta U(\text{fuse})$  is the energy of combustion of the fuse (cotton);  $\Delta_c u^\circ$  is the standard massic energy of combustion.

TABLE 2  
Derived standard ( $p^\circ = 0.1$  MPa) molar values for 2,3-DCNPz in the crystalline phase at  $T = 298.15$  K

Compound	$\Delta_c U_{\text{m}}^\circ(\text{cr})$ $\text{kJ} \cdot \text{mol}^{-1}$	$\Delta_c H_{\text{m}}^\circ(\text{cr})$ $\text{kJ} \cdot \text{mol}^{-1}$	$\Delta_f H_{\text{m}}^\circ(\text{cr})$ $\text{kJ} \cdot \text{mol}^{-1}$
2,3-DCNPz	$-(3080.2 \pm 1.9)$	$-(3076.5 \pm 1.9)$	$429.6 \pm 2.1$

### 3. Experimental results

Table 1 lists the results of combustion experiments for 2,3-DCNPz which correspond to the reaction:



The symbols in this table are as previously described [17]. Samples were ignited at  $T = 298.15$  K, so that

$$\Delta U(\text{IBP}) = -\{\varepsilon_{\text{cal}} + \Delta m(\text{H}_2\text{O}) \cdot c_p(\text{H}_2\text{O}, \text{l}) + \varepsilon_f\} \Delta T_{\text{ad}} + \Delta U_{\text{ign}}, \quad (2)$$

where  $\Delta U(\text{IBP})$  is the energy associated to the isothermal bomb process,  $\Delta m(\text{H}_2\text{O})$  is the deviation of the mass of water added to the calorimeter from 3119.6 g,  $c_p(\text{H}_2\text{O}, \text{l})$  is the specific heat capacity of liquid water,  $\varepsilon_f$  is the energy of the bomb contents after ignition,  $\Delta T_{\text{ad}}$  is the adiabatic temperature raise and  $\Delta U_{\text{ign}}$  is the energy of ignition.

The mean value of all combustion experiments and its standard deviation are also given in table 1, last line.

table 2 lists the derived standard molar energy and enthalpy of combustion,  $\Delta_c U_{\text{m}}^\circ(\text{cr})$  and  $\Delta_c H_{\text{m}}^\circ(\text{cr})$ , and the standard molar enthalpy of formation in crystalline phase  $\Delta_f H_{\text{m}}^\circ(\text{cr})$  at  $T = 298.15$  K for 2,3-DCNPz. In accordance with normal thermochemical practice [22], the uncertainty assigned to the standard molar enthalpy of combustion is twice the overall standard deviation of the mean and includes the uncertainties in calibration. To derive  $\Delta_f H_{\text{m}}^\circ(\text{cr})$  from  $\Delta_c H_{\text{m}}^\circ(\text{cr})$  the standard molar enthalpies of formation of  $\text{H}_2\text{O}(\text{l})$  and  $\text{CO}_2(\text{g})$ , at  $T = 298.15$  K,  $-(285.830 \pm 0.042) \text{ kJ} \cdot \text{mol}^{-1}$  [23] and  $-(393.51 \pm 0.13) \text{ kJ} \cdot \text{mol}^{-1}$  [23], respectively, were used.

Measurements of the standard molar enthalpy of sublimation are given in table 3 with an uncertainty of twice the standard deviation of the mean. The derived standard molar enthalpies of formation, in both the crystalline and gaseous phases, are summarized in table 4.

### 4. Theoretical results and discussion

The geometries of all cyanopyrazines were optimized using the density functional theory (DFT) with the Becke 3-parameter hybrid exchange [24] and Lee–Yang–Parr [25] correlation density functional (B3LYP) and two different basis sets: the 6-31G\* and the 6-311G\*\* [26]. The resulting optimum geometries were further characterized as true minima through construc-

TABLE 3  
Standard ( $p^\circ = 0.1$  MPa) molar enthalpy of sublimation of 2,3-DCNPz, at  $T = 298.15$  K

Compound	No. of expts.	$T/\text{K}$	$\frac{\Delta_g H_{\text{m}}^\circ}{\text{kJ} \cdot \text{mol}^{-1}}$ $\Delta_{\text{cr}, 298.15 \text{ K}}^T H_{\text{m}}^\circ$	$\frac{\Delta_g H_{\text{m}}^\circ}{\text{kJ} \cdot \text{mol}^{-1}}$ $\Delta_{298.15 \text{ K}}^T H_{\text{m}}^\circ(\text{g})$	$\frac{\Delta_g H_{\text{m}}^\circ}{\text{kJ} \cdot \text{mol}^{-1}}$ $\Delta_{\text{cr}}^g H_{\text{m}}^\circ(298.15 \text{ K})$
2,3-DCNPz	6	385	$101.7 \pm 2.7$	12.6	$89.1 \pm 2.7$

TABLE 4

Derived standard ( $p^\circ = 0.1$  MPa) molar enthalpies of formation at  $T = 298.15$  K

Compound	$\Delta_f H_m^\circ(\text{cr})$ $\text{kJ} \cdot \text{mol}^{-1}$	$\Delta_{\text{cr}}^\circ H_m^\circ$ $\text{kJ} \cdot \text{mol}^{-1}$	$\Delta_f H_m^\circ(\text{g})$ $\text{kJ} \cdot \text{mol}^{-1}$
2,3-DCNPz	$429.6 \pm 2.1$	$89.1 \pm 2.7$	$518.7 \pm 3.4$

tion and diagonalization of the B3LYP/6-31G\* Hessian matrices, this procedure providing also the harmonic vibrational frequencies and thermal corrections, which are needed to estimate enthalpies at the temperature of 298.15 K. More accurate energies were also obtained

from single-point calculations at the most stable B3LYP/6-311G\*\* geometries, using the triple-zeta correlation consistent basis set, cc-pVTZ [27]. The obtained electronic energies, zero-point vibrational energies and thermal corrections to  $T = 298.15$  K for all cyanopyrazines are given in table 5. All calculations were performed using the UK version of GAMESS [28,29].

The optimized bond lengths and bond angles of all the cyanopyrazines, obtained using the 6-311G\*\* basis set, are given in table 6 (in figure 1 it is shown the numbering of the atoms). We can see from this table that the successive introduction of the cyano group in the pyrazine ring does not significantly changes the geometry

TABLE 5

Calculated electronic energies (hartree), zero-point vibrational energies and thermal corrections to  $T = 298.15$  K

Compound	$E_{\text{B3LYP/6-31G}^*}$ $\text{kJ} \cdot \text{mol}^{-1}$	$E_{\text{B3LYP/6-311G}^{**}}$ $\text{kJ} \cdot \text{mol}^{-1}$	$E_{\text{ZP/B3LYP/6-31G}^*}$ $\text{kJ} \cdot \text{mol}^{-1}$	$E_{\text{total/B3LYP/6-31G}^*}^a$ $\text{kJ} \cdot \text{mol}^{-1}$	$E_{\text{cc-pVTZ}}$ $\text{kJ} \cdot \text{mol}^{-1}$
Pz <sup>b</sup>	−264.317226	−264.384453	202.27	213.23	−264.413696
CNPz	−356.553721	−356.644265	197.75	213.25	−356.682095
2,3-DCNPz	−448.783915	−448.897549	192.68	212.93	−448.943876
2,5-DCNPz	−448.786910	−448.900760	192.86	213.08	−448.947150
2,6-DCNPz	−448.786211	−448.900046	192.78	213.05	−448.946477
TriCNPz	−541.013980	−541.150856	187.36	212.53	−541.205745
TetraCNPz	−633.239331	−633.399144	181.88	211.98	−633.462512

<sup>a</sup>  $E_{\text{total}} (T = 298.15 \text{ K}) = E_{\text{trans}} + E_{\text{rot}} + E_{\text{ZP}} + E_{\text{vib}}$ .

<sup>b</sup> These calculational results were taken from reference [5].

TABLE 6

Calculated B3LYP/6-311G\*\* bond lengths (nm) and bond angles (°) of the cyanopyrazines

	Pyz <sup>a</sup>	CNPz	2,3-DCNPz	2,5-DCNPz	2,6-DCNPz	TriCNPz	TetraCNPz
1-2	1.335	1.340	1.338	1.339	1.336	1.337	1.332
2-3	1.395	1.401	1.411	1.404	1.404	1.414	1.416
3-4	1.335	1.331	1.338	1.327	1.331	1.333	1.332
4-5	1.335	1.334	1.329	1.339	1.330	1.334	1.332
5-6	1.394	1.397	1.399	1.404	1.404	1.406	1.416
6-1	1.335	1.330	1.329	1.327	1.335	1.326	1.332
2-7		1.438	1.436	1.437	1.438	1.435	1.435
7-8		1.153	1.153	1.153	1.153	1.153	1.153
3-9			1.436			1.436	1.435
9-10			1.153			1.153	1.153
5-11				1.437		1.436	1.435
11-12				1.153		1.153	1.153
6-13					1.438		1.435
13-14					1.153		1.153
1-2-3	122.0	122.2	121.4	122.1	122.1	121.2	121.0
2-3-4	122.0	121.5	121.3	121.5	121.5	121.4	121.0
3-4-5	115.9	116.4	116.8	116.4	116.9	116.8	118.0
4-5-6	122.1	122.0	121.9	122.0	122.1	121.9	121.0
5-6-1	122.0	122.0	121.9	121.5	122.1	121.4	121.0
6-1-2	115.9	115.9	116.8	116.4	115.9	117.3	118.0
1-2-7		117.8	117.3	117.8	117.8	117.4	117.7
2-7-8		177.9	179.6	177.9	177.6	179.5	179.0
2-3-9			121.4			121.4	121.3
3-9-10			179.6			179.3	179.0
4-5-11				117.9		117.9	117.7
5-11-12				177.9		177.6	179.0
5-6-13					120.0		121.3
6-13-14					177.6		179.0

<sup>a</sup> These values were taken from reference [5].

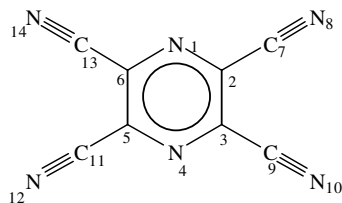


FIGURE 1. Atom numbering scheme of the cyanopyrazines.

of the pyrazine ring. The B3LYP/6-311G\*\* calculated C–(CN) bond lengths vary from 1.435 to 1.438 nm and the C≡N bond lengths are in all molecules of 1.153 nm.

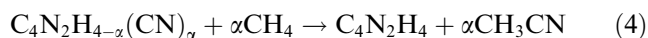
We have previously studied the geometries of the three cyanophenol isomers at the RHF/6-31G\* level [30] and presently we have recalculated these geometries at the B3LYP/6-311G\*\* level. The calculated C<sub>b</sub>–(CN) bond lengths are 1.426 nm (2-), 1.432 nm (3-) and 1.429 nm (4-), and the C≡N bond lengths are 1.157 nm (2-), 1.154 nm (3-) and 1.155 (4-) nm. Comparing the geometries of the cyanopyrazines and cyanophenols the small increase of the bond length C–C(N) in cyanopyrazines seems to be related with the fact that the electronic delocalization between the cyano group (strong  $\sigma$  and  $\pi$  electron acceptor) and the comparatively  $\pi$  electron deficient pyrazine ring must be less effective than in the case of the phenolic ring. In the 2- and 4-cyanophenols the C≡N bond is lengthened because of the allowed resonance structures involving  $=C=N^-$ .

We can see from the energetic results that 2,3-dicyanopyrazine is the least stable dicyanopyrazine isomer which is probably due to the electrostatic repulsions between groups in adjacent positions. This phenomenon was also observed in the dicyanobenzene isomers by Roux *et al.* [31].

Using literature values for the enthalpies of formation [32] of benzene and benzene derivatives we find that the enthalpic increment for the introduction of the cyano group in benzene is of  $(133.1 \pm 2.2)$  kJ · mol<sup>-1</sup> whereas in the pyrazine is of  $(160.7 \pm 2.4)$  kJ · mol<sup>-1</sup>. From these values a higher destabilization of  $(27.6 \pm 3.3)$  kJ · mol<sup>-1</sup> due to substitution is found in pyrazine, which seems not surprising considering that we are looking to the entrance of an electron withdrawing group into an electron deficient pyrazine ring. The same reasoning when we consider the entrance of two cyano groups in adjacent positions of both pyrazine and benzene results in a destabilization of  $(37.7 \pm 4.0)$  kJ · mol<sup>-1</sup> in the pyrazine system.

In order to estimate theoretically the enthalpies of formation of the cyanopyrazines we have further calculated the energy at  $T=0$  K and enthalpy at  $T=298.15$  K of the following two types of reactions:

The first one (type I):



and the second one (type II):

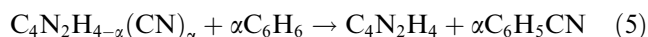


TABLE 7

Calculated reaction (type I) energies, at  $T=0$  K, enthalpies, at  $T=298.15$  K and standard enthalpies of formation in the gas phase, at  $T=298.15$  K

Compound	$\Delta_r E_{T=0} \text{ K}/(\text{kJ} \cdot \text{mol}^{-1})$			$\Delta_r H_{T=298.15 \text{ K}}^\circ/(\text{kJ} \cdot \text{mol}^{-1})$			$\Delta_f H_m^\circ(\text{g})/(\text{kJ} \cdot \text{mol}^{-1})$			exp. <sup>a</sup>
	6-31G*	6-311G**	cc-pVTZ	6-31G*	6-311G**	cc-pVTZ	6-31G*	6-311G**	cc-pVTZ	
CNPz	-0.1	-2.7	-4.4	2.9	0.3	-1.4	341.6	344.1	345.8	$356.8 \pm 2.0^b$
2,3-DCNPz	-16.8	-22.5	-26.2	-10.5	-16.2	-19.9	503.4	509.1	512.7	$518.7 \pm 3.4$
2,5-DCNPz	-8.9	-14.1	-17.6	-2.8	-7.9	-11.4	495.7	500.8	504.3	
2,6-DCNPz	-10.8	-16.0	-19.3	-4.6	-9.8	-13.1	497.5	502.6	506.0	
TriCNPz	-33.8	-42.3	-47.7	-24.1	-32.6	-38.0	665.4	673.9	679.3	
TetraCNPz	-63.2	-75.2	-82.6	-49.9	-62.0	-69.4	839.7	851.7	859.1	

<sup>a</sup> The experimental values of the enthalpies of formation of auxiliary molecules were taken from reference [32].

<sup>b</sup> The standard molar enthalpy of formation of cyanopyrazine was taken from reference [7].

TABLE 8

Calculated reaction (type II) energies, at  $T=0$  K, enthalpies, at  $T=298.15$  K and standard enthalpies of formation in the gas phase, at  $T=298.15$  K

Compound	$\Delta_r E_{T=0} \text{ K}/(\text{kJ} \cdot \text{mol}^{-1})$			$\Delta_r H_{T=298.15 \text{ K}}^\circ/(\text{kJ} \cdot \text{mol}^{-1})$			$\Delta_f H_m^\circ(\text{g})/(\text{kJ} \cdot \text{mol}^{-1})$			Exp. <sup>a</sup>
	6-31G*	6-311G**	cc-pVTZ	6-31G*	6-311G**	cc-pVTZ	6-31G*	6-311G**	cc-pVTZ	
CNPz	-18.6	-16.4	-17.1	-17.5	-15.4	-16.0	349.9	347.8	348.4	$356.8 \pm 2.0^b$
2,3-DCNPz	-53.6	-50.0	-51.5	-51.2	-47.5	-49.1	520.0	516.3	517.9	$518.7 \pm 3.4$
2,5-DCNPz	-45.8	-41.5	-42.9	-43.5	-39.2	-40.6	512.3	508.0	509.4	
2,6-DCNPz	-47.6	-43.4	-44.7	-45.3	-41.1	-42.4	514.1	509.9	511.2	
TriCNPz	-89.1	-83.4	-85.7	-85.2	-79.6	-81.8	690.4	684.8	687.0	
TetraCNPz	-136.9	-130.1	-133.3	-131.4	-124.6	-127.8	873.0	866.2	869.4	

<sup>a</sup> The experimental values of the enthalpies of formation of auxiliary molecules were taken from reference [32].

<sup>b</sup> The standard molar enthalpy of formation of cyanopyrazine was taken from reference [7].



These reactions were chosen to be of the isodesmic type, that is, the number of bonds of any formal type is conserved in each side of the equations and are likely to largely cancel the correlation errors in reactants and products, thus leading to reliable estimates of the reaction energies. These represent in each case the energetic effect of the cyano group on the pyrazine ring relative to its effect on the stability of methane (for type I) and of benzene (for type II). The energies of all auxiliary molecules have been obtained using the same calculation procedure described for the cyanopyrazines and since these are well studied experimentally [32] we are able to estimate the enthalpies of formation of the cyanopyrazines. All theoretical estimates are presented in tables 7 and 8. We can see from the results in these tables that the successive cyano substitutions in pyrazine lead to increasing values for the enthalpic increments. This seems to mean that the third substitution has a higher destabilization component than the second and the fourth substitution more than the third substitution.

The theoretical estimates of the enthalpies of formation obtained using the type II reaction are in much better agreement with the experimental observed ones, the largest error obtained being of only  $8 \text{ kJ} \cdot \text{mol}^{-1}$ , than those obtained from type I. This is probably due to a better cancellation of the correlation errors as hybridization also cancels.

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