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Experimental study of the energetics of tetradentate N_2O_2 Schiff bases derived from salicylaldehyde

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Abstract

The standard ($p^0 = 0.1$ MPa) molar enthalpies of formation, at $T = 298.15$ K, in the gaseous phase of two Schiff bases, *N*,*N*′-bis(salicylaldehydo)ethylenediimine and *N*,*N*′-bis(salicylaldehydo)tetramethylenediimine, were determined from their enthalpies of combustion and sublimation, obtained by static bomb calorimetry in oxygen and by the Knudsen effusion technique, respectively. The enthalpies of fusion of both compounds have been determined by differential scanning calorimetry.

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Keywords: Thermochemistry; Enthalpy of formation; Enthalpy of sublimation; *N*,*N*′-bis(salicylaldehydo)ethylenediimine; *N*,*N*′-bis(salicylaldehydo)tetramethylenediimine

1. Introduction

Thermochemical properties of Schiff bases have attracted our attention in view of their ability to coordinate metal ions, acting as bidentate or tetradentate ligands in metal chelates involving a NO or N_2O_2 donor atom sets. These Schiff base-metal derivatives have considerable interest due to their role as model complexes to biological systems, contributing to the knowledge of their structure and behaviour [1,2]. We have previously reported results for the energetic study of some Schiff bases derived from β-diketones and amines [3] or diamines [4] and their complexes [5,6].

We are now involved in the thermochemical study of another set of related tetradentate Schiff bases, obtained as condensation products of salicylaldehyde with alkyldiamines, and their first row transition metal complexes. Indeed, one of the most important synthetic ligand systems, especially in the context of asymmetric catalysis, includes compounds as *N*,*N*′-bis(salicylaldehydo)ethylenediimine and their metallic complexes, whose synthesis and characterization has been increased, considering their value as catalysts [7–9].

In order to study the energetics of the metal–ligand binding in metal chelates involving Schiff bases, we need to know the enthalpies of formation, in the gaseous state, of the parent ligands. In this work we present the enthalpies of formation, determined by static bomb calorimetry, and the standard molar enthalpies of sublimation, measured by the Knudsen effusion technique, of two crystalline *N*,*N*′-bis(salicylaldehydo)alkyldiimine derivatives, *N*,*N*′-bis(salicylaldehydo)ethylenediimine (H_2salen) and *N*,*N*′-bis(salicylaldehydo)tetramethylenediimine (H_2salbuten), represented in Fig. 1. The results obtained were used to derive the standard molar enthalpies of formation of the gaseous species.

2. Experimental

2.1. Synthesis and characterization of compounds

The compounds *N*,*N*′-bis(salicylaldehydo)ethylenediimine, $C_{16}H_{16}N_2O_2$ (H_2salen), and *N*,*N*′-bis(salicylaldehydo)tetramethylenediimine, $C_{18}H_{20}N_2O_2$ (H_2salbuten), were

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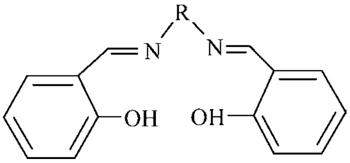


Fig. 1. Molecular structure of H_2salen and H_2salbuten. R = $(CH_2)_2$, *N*,*N*′-bis(salicylaldehydo)ethylenediimine, H_2salen; R= $(CH_2)_4$, *N*,*N*′-bis(salicylaldehydo)tetramethylenediimine, H_2salbuten.

prepared according to previously published methods [10], by refluxing 0.05 mol of salicylaldehyde (Merck-Schuchard, purified by distillation) and 0.025 mol of diamine (ethylenediamine or 1,4-butanediamine, Aldrich Chemie, 99%, purified by distillation) in 30 cm [3] of dried ethanol, for 30 min and cooling the reaction mixture. The Schiff bases were separated as yellow needles and were recrystallized twice from methanol (yield 75–80%). The compounds are stable at room temperature and have been characterized by i.r. spectroscopy and elemental analysis. The microanalytical results (Microanalytical Services of the University of Manchester) for the mass fractions w of C, H and N were as follows: for H_2salen, $C_{16}H_{16}N_2O_2$, found $10^2\,w(C) = 71.30$, $10^2\,w(H) = 6.08$, $10^2\,w(N) = 10.36$, calculated $10^2\,w(C) = 71.62$, $10^2\,w(H) = 6.01$, $10^2\,w(N) = 10.44$; for H_2salbuten, $C_{18}H_{20}N_2O_2$, found $10^2\,w(C) = 72.98$, $10^2\,w(H) = 6.83$, $10^2\,w(N) = 10.50$, calculated $10^2\,w(C) = 72.95$, $10^2\,w(H) = 6.80$, $10^2\,w(N) = 10.80$.

The compounds H_2salen and H_2salbuten were studied by DSC over the temperature range of 323–413 and 323–383 K, respectively, and no phase transitions were found before the melting temperatures (melting points and enthalpies of fusion are, respectively: for H_2salen, 397.9 K and 34.09 ± 0.19 kJ mol^{-1}; for H_2salbuten, 362.8 K and 35.54 ± 0.15 kJ mol^{-1}). The temperature range of the supplementary effusion measurements are shown to be below the melting ranges.

2.2. Combustion calorimetry

The combustion experiments were performed with a static bomb calorimeter, with a twin valve bomb, type 1108, Parr Instrument Company [11,12]. For the study of H_2salen, the calorimeter was calibrated with benzoic acid (Bureau of Analysed Samples, Thermochemical Standard, BCS-CRM-190n), whose massic energy of combustion is $-(26433.0 \pm 3.9)\,\mathrm{J\,g^{-1}}$, under certificate conditions. From nine calibration experiments, $\varepsilon(\mathrm{calor}) = 16000.2 \pm 1.7\,\mathrm{J\,K^{-1}}$, where the uncertainty quoted is the standard deviation of the mean. Before starting the study of H_2salbuten, several changes were made to the calorimeter, resulting in changes to ε(calor). From nine calibration experiments, using another sample of benzoic acid (Thermochemical Standard, BCS-CRM-190p) with the massic energy of combustion $-(26431.8 \pm 3.7)\,\mathrm{J\,g^{-1}}$, resulted $\varepsilon(\mathrm{calor}) = 16017.0 \pm 1.3\,\mathrm{J\,K^{-1}}$, where the uncertainty quoted is also the standard deviation of the mean. In both cases ε(calor) was corrected for an average mass of water of 3119.6 g added to the calorimeter.

For all experiments, ignition was made at $T = 298.150 \pm 0.001$ K. Combustion experiments were performed in oxygen at $p = 3.04$ MPa, with 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, empirical formula $CH_{1.686}O_{0.843}$, $\Delta_c u^\circ = -16250\,\mathrm{J\,g^{-1}}$ [13]: this value was confirmed in our laboratory. The corrections for nitric acid formation were based on $-59.7\,\mathrm{kJ\,mol^{-1}}$ [14], for the molar energy of formation of 0.1 mol dm^{-3} HNO_3(aq) from N_2, O_2, and H_2O(l). The amount of substance used in each experiment was determined from the total mass of carbon dioxide produced, after allowance was made for that formed from the cotton-thread fuse. The densities at $T = 298.15$ K for H_2salen and H_2salbuten were estimated as $\rho = 1.0\,\mathrm{g\,cm^{-3}}$. An estimated pressure coefficient of massic energy: $(\partial u/\partial p)_T = -0.2\,\mathrm{J\,g^{-1}\,MPa^{-1}}$, at $T = 298.15$ K, a typical value for most organic compounds, was assumed. For each compound, the massic energy of combustion $\Delta_c u^\circ$ was calculated by the procedure given by Hubbard et al. [15]. The relative atomic masses used throughout this paper were those recommended by the IUPAC Commission in 1999 [16].

2.3. Enthalpies of sublimation

The standard molar enthalpies of sublimation of H_2salen and H_2salbuten were determined by the Knudsen effusion method using the apparatus as described by Burkinshaw and Mortimer [17], with the detailed modifications previously reported [18]. The equipment was tested with several compounds of known standard molar enthalpies of sublimation (benzanthrone, squaric acid, and 4-hydroxy-2-methylquinoline) and good agreement with the literature values was obtained. The vapour effusing from the Knudsen cell was allowed to condense on a quartz crystal positioned above the effusion hole; changes in the frequency Δf of oscillation of the quartz crystal were proportional to the mass condensed in its surface [19], $\Delta f = C_f \Delta m$, where C_f is a proportionality constant.

From the Knudsen equation:

$$p = \left(\frac{\Delta m}{\Delta t}\right) a^{-1} \left(\frac{2\pi RT}{M}\right)^{1/2}, \qquad (1)$$

where $(\Delta m/\Delta t)$ is the rate of mass loss, a the effective area of the effusion hole, and M the molar mass of the effusing vapour. As the measured rate of change of frequency of oscillation with time, $\nu = \Delta f/\Delta t$, is directly proportional to the rate of sublimed mass [19] of the crystalline sample, ν

$= \mathrm{C}_f \Delta m/\Delta t$:

$$p = \nu T^{1/2} \frac{(2\pi R/M)^{1/2}}{aC_f}. \qquad (2)$$

By applying the integrated form of the Clausius–Clapeyron equation, the enthalpy of sublimation, $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^{\circ}$, may be derived from the slope (m) of $\ln(\nu T^{1/2})$ against T^{-1}. From at least five independent sets of experimental measurements of the frequency of the quartz oscillator for each complex, at convenient temperature intervals, the enthalpy of sublimation of each compound, referred to the mean temperature of the experimental range, was calculated.

3. Results

3.1. Combustion calorimetry

Results for a typical combustion experiment on each compound are given in Table 1; $\Delta m(\mathrm{H_2O})$ is the deviation of the mass of water added to the calorimeter from 3119.6 g, the mass assigned for $\varepsilon(\mathrm{calor})$; ΔU_{Σ} is the correction to the standard state; the remaining terms are as previously described [15]. As samples were ignited at $T = 298.15\,\mathrm{K}$, $\Delta U(\mathrm{IBP}) = -\{\varepsilon(\mathrm{calor}) + c_p(\mathrm{H_2O,\,l})\Delta m(\mathrm{H_2O}) + \varepsilon_{\mathrm{f}}\}\Delta T_{\mathrm{ad}} + \Delta U(\mathrm{ign})$; where ΔT_{ad} is the calorimeter temperature change corrected for heat exchange and the work of stirring. The individual values of $-\Delta_{\mathrm{c}} u^{\circ}$, together with the mean and its standard deviation, are given in Table 2. Table 3 lists the derived standard molar enthalpies of combustion and of formation, in the condensed state. In accordance with normal thermochemical practice [20], the uncertainties assigned to the standard molar enthalpies of combustion and formation are twice the overall standard deviation of the mean and include the uncertainties in calibration and in the auxiliary quantities used. To derive $\Delta_{\mathrm{f}} H_{\mathrm{m}}^{\circ}(\mathrm{cr})$ from $\Delta_{\mathrm{c}} H_{\mathrm{m}}^{\circ}$ the standard molar enthalpies of formation for $\mathrm{H_2O(l)}$: $-(285.83 \pm 0.04)\,\mathrm{kJ\,mol^{-1}}$ and for $\mathrm{CO_2(g)}$: $-(393.51 \pm 0.13)\,\mathrm{kJ\,mol^{-1}}$, were used [21].

Table 1
Typical combustion experiments for N,N'-bis(salicylaldehydo)ethylenediimine ($\mathrm{H_2}$salen) and N,N'-bis(salicylaldehydo)tetramethylenediimine ($\mathrm{H_2}$salbuten), at $T = 298.15\,\mathrm{K}$

	$\mathrm{H_2}$salen	$\mathrm{H_2}$salbuten
m(cpd) (g)	0.78509	0.74466
m'(fuse) (g)	0.00226	0.00290
ΔT_{ad} (K)	1.53502	1.52440
$\varepsilon_{\mathrm{f}}/\ (\mathrm{J\,K^{-1}})$	15.9	15.96
$\Delta m(\mathrm{H_2O})$ (g)	–	−0.1
$-\Delta U(\mathrm{IBP})$ (J)[a]	24585.0	24442.2
$\Delta U(\mathrm{HNO_3})$ (J)	45.4	42.9
ΔU(ign.) (J)	1.2	1.2
ΔU_{Σ} (J)	16.5	14.7
ΔU(fuse) (J)	36.7	47.1
$-\Delta_{\mathrm{c}} u^{\circ}\ (\mathrm{J\,g^{-1}})$	31187.91	32679.8

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

Table 2
Individual values of the massic energy of combustion, $\Delta_{\mathrm{c}} u^{\circ}$, of N,N'-bis(salicylaldehydo)ethylenediimine ($\mathrm{H_2}$salen) and N,N'-bis(salicylaldehydo)tetramethylenediimine ($\mathrm{H_2}$salbuten), at $T = 298.15\,\mathrm{K}$

$-\Delta_{\mathrm{c}} u^{\circ}\ (\mathrm{J\,g^{-1}})$	
$\mathrm{H_2}$salen	$\mathrm{H_2}$salbuten
31190.7	32697.2
31173.0	32675.4
31167.1	32679.8
31181.5	32691.8
31161.9	32674.8
31187.9	–
31194.2	–
31192.4	–
31181.1 ± 4.4[a]	32683.8 ± 4.5[a]

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

3.2. Sublimation

The results for the determination of the standard molar enthalpies of sublimation of $\mathrm{H_2}$salen and $\mathrm{H_2}$salbuten, by the Knudsen effusion method, are summarized in Tables 4 and 5, respectively, together with the mean temperatures ($\langle T\rangle$) of the experimental ranges and the standard molar enthalpies of sublimation at these mean temperatures, $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^{\circ}\ (\langle T\rangle)$; the parameter of the Clausius–Clapeyron equation corresponding to the slope was obtained using a least square fitting of the experimental data. The value of $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^{\circ}\ (\langle T\rangle)$ was corrected to $T = 298.15\,\mathrm{K}$ assuming $\Delta_{\mathrm{cr}}^{\mathrm{g}} C_{\mathrm{p,m}}^{\circ} = -50\,\mathrm{J\,K^{-1}\,mol^{-1}}$, a value previously estimated for metal complexes [17], to yield $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^{\circ}$ ($\mathrm{H_2}$salen) $= 141.3 \pm 3.2\,\mathrm{kJ\,mol^{-1}}$ and $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^{\circ}$ ($\mathrm{H_2}$salbuten) $= 165.1 \pm 3.1\,\mathrm{kJ\,mol^{-1}}$, where the uncertainties assigned are twice the overall standard deviations of the mean.

Table 6 summarizes the standard molar enthalpies of formation, in both crystalline and gaseous states, as well as the standard molar enthalpies of sublimation, at $T = 298\,\mathrm{K}$, for the Schiff bases studied in this work.

Table 3
Derived standard ($p^0 = 0.1\,\mathrm{MPa}$) molar energies of combustion, $\Delta_{\mathrm{c}} U_{\mathrm{m}}^{\circ}$, standard molar enthalpies of combustion, $\Delta_{\mathrm{c}} H_{\mathrm{m}}^{\circ}$, and standard molar enthalpies of formation, $\Delta_{\mathrm{f}} H_{\mathrm{m}}^{\circ}$, for crystalline N,N'-bis(salicylaldehydo)ethylenediimine ($\mathrm{H_2}$salen) and N,N'-bis(salicylaldehydo)tetramethylenediimine ($\mathrm{H_2}$salbuten), at $T = 298.15\,\mathrm{K}$

	$-\Delta_{\mathrm{c}} U_{\mathrm{m}}^{\circ}$ (cr) $(\mathrm{kJ\,mol^{-1}})$	$-\Delta_{\mathrm{c}} H_{\mathrm{m}}^{\circ}$ (cr) $(\mathrm{kJ\,mol^{-1}})$	$\Delta_{\mathrm{f}} H_{\mathrm{m}}^{\circ}$ (cr) $(\mathrm{kJ\,mol^{-1}})$
$\mathrm{H_2}$salen	8366.4 ± 3.2	8371.4 ± 3.2	−211.4 ± 3.8
$\mathrm{H_2}$salbuten	9686.4 ± 3.4	9693.8 ± 3.4	−247.7 ± 4.1

Table 4
Knudsen effusion results for H_2salen

Exp.	$[T]$ (K)	$\langle T \rangle$ (K)	$(-m \pm \sigma_m)$ (K)	r	$\Delta_{cr}^{g}H_m^\circ\langle T \rangle$ (kJ mol^{-1})	$\Delta_{cr}^{g}H_m^\circ\langle 298.15\,K \rangle$ (kJ mol^{-1})
B	348.2−357.0	352.6	17074.5 ± 405.7	0.9994	141.97 ± 3.37	144.7 ± 3.4
C	351.2−363.2	357.2	17116.2 ± 45.0	0.9999	142.31 ± 0.37	145.3 ± 0.4
D	349.6−361.6	355.6	16540.2 ± 85.0	0.9999	137.52 ± 0.71	140.4 ± 0.7
E	350.2−356.0	353.0	16382.4 ± 446.0	0.9996	136.21 ± 3.71	139.0 ± 3.7
F	351.6−363.4	357.6	16116.8 ± 49.2	0.9999	134.00 ± 0.41	137.0 ± 0.4

$\overline{\Delta_{cr}^{g}H_m^\circ}(298.15\,\mathrm{K}) = 141.3 \pm 3.2\,\mathrm{kJ\,mol^{-1}}$.

Table 5
Knudsen effusion results for H_2salbuten

Exp.	$[T]$ (K)	$\langle T \rangle$ (K)	$(-m \pm \sigma_m)$ (K)	r	$\Delta_{cr}^{g}H_m^\circ\langle T \rangle$ (kJ mol^{-1})	$\Delta_{cr}^{g}H_m^\circ\langle 298.15\,K \rangle$ (kJ mol^{-1})
A	351.8−361.2	356.4	19284.5 ± 440.8	0.9992	160.33 ± 3.66	163.2 ± 3.7
B	349.0−359.2	354.2	19786.9 ± 900.9	0.9959	164.51 ± 7.49	167.3 ± 7.5
C	349.4−359.6	354.6	20191.5 ± 371.1	0.9993	167.88 ± 3.09	170.7 ± 3.1
I	350.0−358.2	354.2	19074.8 ± 279.2	0.9997	158.59 ± 2.32	161.4 ± 2.3
J	352.6−358.8	355.6	19715.9 ± 574.2	0.9992	163.92 ± 4.77	166.8 ± 4.8
L	351.0–359.2	355.2	19059.0 ± 768.4	0.9976	158.46 ± 6.39	161.3 ± 6.4

$\overline{\Delta_{cr}^{g}H_m^\circ}(298.15\,\mathrm{K}) = 165.1 \pm 3.1\,\mathrm{kJ\,mol^{-1}}$.

Table 6
Derived standard ($p^0 = 0.1$ MPa) molar enthalpies of formation, $\Delta_f H_m^\circ$, and standard molar enthalpies of sublimation, $\Delta_{cr}^{g}H_m^\circ$, for *N*,*N*′-bis(salicylaldehydo)ethylenediimine (H_2salen) and *N*,*N*′-bis(salicylaldehydo) tetramethylenediimine (H_2salbuten), at $T = 298.15$ K

	$\Delta_f H_m^\circ$(cr) (kJ mol^{-1})	$\Delta_{cr}^{g}H_m^\circ$ (kJ mol^{-1})	$\Delta_f H_m^\circ$ (g) (kJ mol^{-1})
H_2salen	−211.4 ± 3.8	141.3 ± 3.2	−70.1 ± 5.0
H_2salbuten	−247.7 ± 4.1	165.1 ± 3.1	−82.6 ± 5.1

4. Discussion

The present experimental work represents a first contribution to the study of *N*,*N*′-bis(salicylaldehyde)alkyldiimine derivatives, following previous studies for other bidentate and tetradentate Schiff bases [3,4] derived from β-diketones and their copper(II) and nickel(II) complexes [5,6].

It is difficult to establish a bond-energy scheme for these compounds, as there is not enough information on model compounds, for comparison. It may be interesting to consider the enthalpies of the hypothetical reactions of formation of H_2salen and H_2salbuten, in the gaseous state, from salicylaldehyde and the appropriate diamine, i.e., $\Delta_r H_m^\circ$(g) for Scheme 1; this requires the additional knowledge of the standard enthalpies of formation, in the gaseous state, of water, salicylaldehyde, 1,2-ethanediamine and 1,4-butanediamine.

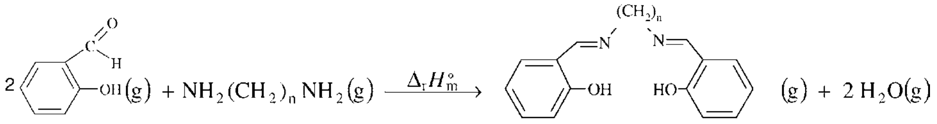
Since there are no published experimental values for the standard enthalpies of formation, in the gaseous state, of salicylaldehyde and of 1,4-butanediamine, they have been estimated, from the following group schemes, using literature values from Pedley et al. [22]:

$$\text{Salicylaldehyde} = \text{2-hydroxybenzoic acid} - \text{benzoic acid} + \text{benzaldehyde}, \tag{3}$$

$$\text{1, 4-Butanediamine} = 2 \times \text{(1-butylamine)} - \text{butane} \tag{4}$$

as $\Delta_f H_m^\circ$ (salicylaldehyde, g) $= -[236.7 \pm 3.8]\,\mathrm{kJ\,mol^{-1}}$ and $\Delta_f H_m^\circ$ ($NH_2(CH_2)_4NH_2$, g) $= -[57.9 \pm 2.3]\,\mathrm{kJ\,mol^{-1}}$. With these estimates and the literature values of $\Delta_f H_m^\circ$ $\{NH_2(CH_2)_2NH_2,\ g\} = -(18.0 \pm 0.7)\,\mathrm{kJ\,mol^{-1}}$ [22] and $\Delta_f H_m^\circ$ (H_2O, g) $= -(241.82 \pm 0.04)\,\mathrm{kJ\,mol^{-1}}$ [21] from Scheme 1, the enthalpies of reaction in the gaseous phase, $\Delta_r H_m^\circ$(g), for the formation of H_2salen and H_2salbuten are calculated, respectively, as $-(62.3 \pm 9.1)$ and $-(34.9 \pm 9.4)\,\mathrm{kJ\,mol^{-1}}$.

The values of the enthalpies of the reactions of formation of the Schiff bases from the salicylaldehyde and the diamines, show a clear dependence on the number of methy-



n = 2: 1,2-ethanediamine; n = 4: 1,4-butanediamine.

Scheme 1.

lene groups in the Schiff base, with the enthalpy of reaction increasing with the number of methylene groups.

An alternative method to evaluate the relation between the experimental enthalpies of formation of H_2salen and H_2salbuten can be obtained considering the hypothetical gaseous reaction (5), whose enthalpy is $\Delta_r H_m^\circ(g) = +(27.4 \pm 7.5)\,\mathrm{kJ\,mol^{-1}}$:

$$\mathrm{H_2salen(g) + NH_2(CH_2)_4NH_2(g) \rightarrow H_2salbuten(g) + NH_2(CH_2)_2NH_2(g)} \quad (5)$$

The enthalpy of reaction for the formation of H_2salen can be compared with those observed for the formation of other Schiff Bases derived from similar condensation reactions between ethylenediamine and β-diketones [4]. The enthalpy obtained for the formation reaction of H_2salen, $\Delta_r H_m^\circ(g) = -(62.3 \pm 9.1)\,\mathrm{kJ\,mol^{-1}}$, is similar to that one obtained [4] for the formation of H_2acacen, $\Delta_r H_m^\circ(g) = -(56.9 \pm 4.2)\,\mathrm{kJ\,mol^{-1}}$, but $20\,\mathrm{kJ\,mol^{-1}}$ higher than the one obtained for H_2bzacen, $\Delta_r H_m^\circ(g) = -(82.3 \pm 9.3)\,\mathrm{kJ\,mol^{-1}}$, what is coherent with the greater delocalisation found for this compound.

These experimental thermochemical data are coherent among them, but further support for the interpretation of the energetic behaviour of Schiff bases needs complementary data on other compounds of this type.

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