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Study of Energetics and Structure of 1,2,3-Benzotriazin-4(3H)-one and its 1H and Enol Tautomers

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Ⓢ Supporting Information

ABSTRACT: This paper reports an experimental and computational study on the energetics of 1,2,3-benzotriazin-4(3H)-one. The standard ($p° = 0.1$ MPa) molar enthalpy of formation of solid 1,2,3-benzotriazin-4(3H)-one, at $T = 298.15$ K, was derived from its standard massic energy of combustion measured by static bomb combustion calorimetry in oxygen. The Calvet high-temperature vacuum sublimation technique was

1,2,3-benzotriazin-4(3H)-one   1,2,3-benzotriazin-4(1H)-one   1,2,3-benzotriazin-4-ol

used to measure the respective standard molar enthalpy of sublimation at $T = 298.15$ K. From these two experimentally determined thermodynamic parameters, we have calculated the standard molar enthalpy of formation of 1,2,3-benzotriazin-4(3H)-one in the gas phase at $T = 298.15$ K, (200.9 ± 3.8) kJ·mol^{-1}. Interrelations between structure and energy for 1,2,3-benzotriazin-4(3H)-one, the tautomer 1,2,3-benzotriazin-4(1H)-one, and the enol tautomer 1,2,3-benzotriazin-4-ol were discussed based on density functional theory (DFT) calculations with the B3LYP hybrid functional and the 6-311++G(d,p) basis set. The gas-phase enthalpy of formation of 1,2,3-benzotriazin-4(3H)-one was estimated from quantum chemical calculations using the G3(MP2)//B3LYP composite method. Nucleus-independent chemical shifts (NICS) were also calculated with the purpose of analyzing the aromaticity of the benzenic and heterocyclic rings of the title molecule and others related tautomerically to it.
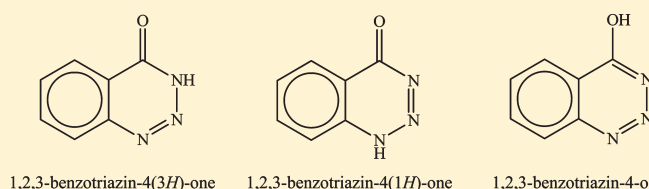
1. INTRODUCTION

1,2,3-Benzotriazine is a two-ring nitrogen containing heterocycles formally related to quinoline and isoquinoline, cinnoline and phthalazine, and quinazoline and quinoxaline with their two-constituent fused six-membered rings, namely, pyridine, pyridazine, pyrimidine, and pyrazine. 1,2,3-Benzotriazine forms a variety of derivatives such as 4-oxo derivative 1,2,3-benzotriazin-4-one, much as the aforementioned species form derivatives such as 2- and 4-quinolinone. It is not surprising that benzotriazin-4-one derivatives are known to possess various important biomedical activities. The parent species has been shown to have sedative properties,[1] while the 7-chloro-3-methyl-6-sulfamyl derivative is a diuretic.[2] Some oxo-dialkylaminoethyl benzotriazinoneacetamide derivatives are local anesthetics,[3] while benzotriazinone-substituted pyrazole-4-acetic acids exhibit anti-inflammatory and analgesic behavior.[4] 3-Imidazol-1-yl-propyl and 4-imidazol-1-yl-butyl-1,2,3-benzotriazin-4-one are antihypertensives.[5] Some of the related thione derivatives have antifungal activity.[6] We will not attempt to explain the diverse interactions that account for these activities. Rather, even if we return to the thermochemically unstudied parent species 1,2,3-benzotriazin-4-one, we immediately note complications. It is to be noted that it is normally drawn as molecule (I). However, it has a tautomer with the hydrogen atom at N-1 instead of N-3, molecule (II), and its enol tautomer (III) that

plausibly impact its stability and both chemical and biomedical reactivity.

(I)   (II)   (III)
1,2,3-benzotriazin-4(3H)-one   1,2,3-benzotriazin-4(1H)-one   1,2,3-benzotriazin-4-ol
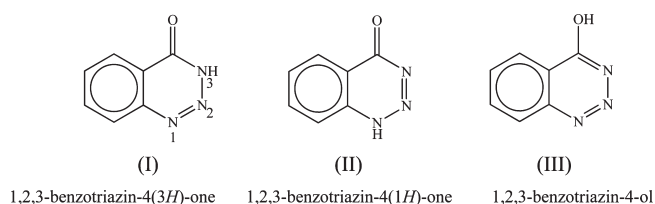
For guidance, we might consider the one-ring constituent, 1,2,3-triazine, and perchance its derivatives. However, unlike pyrimidines and pyrazines,[7−13] there are no thermochemical data for any 1,2,3-triazine derivative at all, with one ring or two, with or without an appended keto group. The current calorimetric and quantum chemical computational study ameliorates this deficiency, in our opinion, for 1,2,3-benzotriazine derivatives; we know of no accessible 1,2,3-triazine derivative to aid us with direct understanding of the one-ring system.

1,2,3-Benzotriazin-4-one has, for long, been known to exist in the 3H-form as its predominant tautomer.[14] A ^{15}N NMR

investigation[15] of a series of benzotriazinones has shown that a hydrogen atom is bonded to N-3, which confirms that these molecules do indeed exist in the tautomeric form (I) rather than the alternative tautomer (II). A diffractometric study[16] of the crystal and molecular structure of 1,2,3-benzotriazin-4-one has also concluded that the hydrogen atom is bonded to N-3.

We have already studied similar heterocyclic compounds in which a benzene ring is fused to a six-membered ring containing nitrogen and/or oxygen and affixed carbonyl groups, 2H-1,4-benzoxazine-3(4H)one,[17] 2H-1,3-benzoxazine-2,4(3H)dione, and 2H-3,1-benzoxazine-2,4(1H)dione (isatoic anhydride),[18] coumarin and chromone,[19] and chromanone, 3-isochromanone, and dihydrocoumarin.[20] A new model of aromaticity for these compounds derived from heterocycles with five-membered rings provides a language for understanding the relative stability of the two benzotriazinones.[21]

In the present work, we report the standard molar enthalpy of formation of 1,2,3-benzotriazin-4(3H)-one at T = 298.15 K in the solid and gaseous phases. These thermochemical parameters were obtained using the static bomb combustion calorimetry and microcalorimetry Calvet techniques. Computational calculations performed for the three tautomers 1,2,3-benzotriazin-4(3H)-one, 1,2,3-benzotriazin-4(1H)-one, and 1,2,3-benzotriazin-4-ol, using density functional theory with the B3LYP functional and the 6-311++G(d,p) basis set, allowed us to establish the energetically most stable tautomer, 1,2,3-benzotriazin-4(3H)-one. The respective standard molar enthalpy of formation in the gaseous phase at T = 298.15 K was estimated from computational calculations using the G3(MP2)//B3LYP composite method and appropriately chosen reactions. A comparison of the aromaticity of 1,2,3-benzotriazin-4(3H)-one and its tautomers, using NICS values measured at the benzenic and heterocyclic rings, is also reported.

2. EXPERIMENTAL METHODS

2.1. Material. 1,2,3-Benzotriazin-4(3H)-one was obtained commercially from Sigma-Aldrich Co. [CAS 90-16-4] with the assigned purity of 99.8% determined by HPLC and was further purified by repeated vacuum sublimation before the calorimetric study. The compositional purity of the samples and the completeness of the combustion process were confirmed through the carbon dioxide recovery ratios determined after the combustion experiments (see section 2.2). 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 (99.98 ± 0.02). The purity compound could not be assessed by differential scanning calorimetry (DSC) as this compound decomposes in the fusion process. The specific density, used to calculate the mass from the apparent mass in air, was estimated from the mass and the dimension of the pellets as $\rho = 0.96$ g·cm^{-3}. The relative atomic masses used throughout this paper were those recommended by the IUPAC Commission.[22]

2.2. Combustion Calorimetry. The energy of combustion of 1,2,3-benzotrizin-4(3H)-one was measured using a static bomb calorimeter. Because the apparatus and the technique have been described,[23,24] only a brief description will be given here. The energy equivalent of the calorimeter was determined from the combustion of benzoic acid BDH Thermochemical Standard, batch 69376/01, certificated in Manchester University, having a massic energy of combustion of $\Delta_c u = -(26435.1 \pm 3.5)$ J·g^{-1}, under certificate conditions. Calibration experiments were carried out in oxygen at the pressure 3.04 MPa in the presence of 1.00 cm^3 of deionized water. One set of seven calibration experiments was performed, leading to the value of the energy equivalent of the calorimeter, $\varepsilon_{cal} = (16005.0 \pm 2.0)$ J·K^{-1}, where the uncertainty quoted is the standard deviation of the mean.

Solid samples of 1,2,3-benzotriazin-4(3H)-one were burned in the pellet form through a cotton thread fuse in oxygen at a pressure of 3.04 MPa and with 1.00 cm^3 of deionized water added to the bomb. For all experiments, the calorimeter's temperature was 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. The ignition of the samples was made at T = (298.150 ± 0.001) K by the discharge of a 1400 μF capacitor through a platinum ignition wire. At least 100 readings were taken for the initial period, and 200 readings were taken for the main and final periods. The mass of the compound, m(cpd), used in each experiment was determined from the total mass of carbon dioxide, m(CO$_2$,total), produced in the experiments, taking into account that formed from the combustion of the cotton thread fuse. The amount of nitric acid produced during the experiments was quantified by titration of the aqueous solution that resulted from washing the inside of the bomb.

2.3. Microcalorimetry Calvet. The standard molar enthalpy of sublimation was measured using the vacuum sublimation drop microcalorimetric technique.[25] Analytically weighted samples of the solid compound (about 3 mg) contained in a small thin glass capillary tube sealed at one end and a blank capillary were simultaneously dropped at room temperature into the hot reaction vessels in the Calvet high-temperature microcalorimeter (Setaram, Lyon, France) held at the convenient temperature T and were then removed from the hot zone by vacuum sublimation. The thermal corrections for the glass capillary tubes were determined in separate experiments and were minimized, as far as possible, by dropping tubes of nearly equal mass, to within ± 10 μg, into each of the twin calorimeter cells. The microcalorimeter was calibrated in situ using the reported standard molar enthalpy of sublimation of naphthalene, $\Delta_{cr}^{g}H_m^{\circ}(298.15\,\text{K}) = (72.600 \pm 0.600)$ kJ·mol^{-1},[26] a primary reference material. Accuracy tests were performed with benzoic acid, $\Delta_{cr}^{g}H_m^{\circ}(298.15\,\text{K}) = (89.700 \pm 1.000)$ kJ·mol^{-1}.[26]

3. COMPUTATIONAL DETAILS

The geometries of 1,2,3-benzotriazin-4(3H)-one and its tautomers were fully optimized using density functional theory (DFT) with the hybrid functional B3LYP and two basis sets, 6-31G(d) and 6-311G++(d,p). The B3LYP density functional is a combination of Becke's 3-parameter nonlocal hybrid exchange potential[27] with the nonlocal correlation functional of Lee, Yang, and Parr (LYP).[28] The B3LYP/6-31G(d) geometries were further certified as true minima by construction and diagonalization of the Hessian matrices at the same level of theory. This procedure also provides the harmonic vibrational frequencies that, after scaling by an appropriate factor of 0.9613,[29] allow the calculation of the thermal corrections needed to derive energies at a temperature of 298.15 K. In order to obtain better estimates of the molecular energies, calculations were carried out using the G3(MP2)//B3LYP method.[30] From these calculations and using appropriate reactions, the standard molar enthalpy of formation of 1,2,3-benzotriazin-4(3H)-one at T = 298.15 K was derived.

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Table 1. Combustion Experiment Results of 1,2,3-Benzotriazin-4($3H$)-one at T = 298.15 K^a

$m(CO_2$, total$)$/g		1.63019	0.93384	1.19038	1.37604	1.39826
$m(cpd)$/g	0.72831	0.77686	0.44423	0.56671	0.65536	0.66616
$m(fuse)$/g	0.00248	0.00224	0.00230	0.00236	0.00239	0.00215
ΔT_{ad}/K	1.10700	1.18159	0.67633	0.86228	0.99607	1.01348
ε_f/(J·K^{-1})	15.46	15.22	14.80	14.92	15.11	15.27
$\Delta m(H_2O)$/g	0.1	−0.1	−0.1	−0.2	−0.1	0.1
$-\Delta U(IBP)$/J	17733.91	18927.64	10833.20	13811.74	15955.54	16235.44
$-\Delta U(HNO_3)$/J	56.89	62.69	36.89	50.15	48.77	58.33
$-\Delta U(carbon)$/J	0.00	0.00	0.00	0.00	0.00	0.00
$\Delta U(ign)$/J	1.20	1.20	1.19	1.20	1.19	1.21
$-\Delta U_\Sigma$/J	16.39	17.53	9.78	12.54	14.70	14.84
$-\Delta U(fuse)$/J	40.28	36.38	37.35	38.33	38.81	34.92
$-\Delta_c u°$/(J·g^{-1})	24193.48	24214.20	24197.33	24193.54	24190.16	24209.42

$\langle\Delta_c u°\rangle$ = −(24199.7 ± 4.0) J·g^{-1} (0.017%)

^{a} Parameters: $m(CO_2$, total$)$ is the total mass of CO_2 formed in the experiment; $m(cpd)$ is the mass of compound burnt in the experiment; $m(fuse)$ is the mass of fuse (cotton) used in the experiment; 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 the mass of water added to the calorimeter from 3119.6 g; $\Delta U(IBP)$ is the energy change for the isothermal combustion reaction under actual bomb conditions, $\Delta U(IBP)$ includes $\Delta U(ign)$; $\Delta U(HNO_3)$ is the energy correction for the nitric acid formation; $\Delta U(carbon)$ is the energy correction for carbon formation; $\Delta U(ign)$ is the energy of combustion of the fuse; ΔU_Σ is the energy correction to the standard state; $\Delta U(fuse)$ is the energy of combustion of the fuse (cotton); $\Delta_c u°$ is the standard massic energy of combustion.

The aromatic behavior of molecules can be assessed on the basis of the analysis of their magnetic properties, namely, the observable effects of the circular ring current induced by applied external magnetic fields. For aromatic systems, such currents produce an induced magnetic field opposing the external one, a phenomenon which can be experimentally probed by the nuclear magnetic resonance (NMR) chemical shifts measured at each nucleus. This concept has been generalized and converted into a useful aromaticity index by Schleyer et al.,[31] who developed a methodology involving the calculation of the chemical shifts not just at every nucleus but at any point in the space in the vicinity of molecules, leading to what is now described as nucleus-independent chemical shifts (NICS); these are just the negative of the isotropic component (the trace) of the chemical shielding tensor evaluated at the specific points. Aromaticity has then been very often assessed by calculating the NICS at the geometric center of the rings and also, to avoid the shielding effects of the framework of σ electrons, at some point somewhat (generally 1.0 Å) above the geometric center of the ring.[32,33]

Significantly negative (shielded) NICS values inside of rings are due to induced diatropic ring currents and denote aromaticity, whereas positive (deshielded) values denote paratropic ring currents associated with antiaromatic behavior. Additionally, it has also been recognized that because ring currents resulting from cyclic π-electron delocalization are induced primarily by the external magnetic field applied perpendicularly to the ring (conventionally the ZZ direction), the out-of-plane (ZZ) component of the magnetic shielding tensor should contain the most relevant information for the aromaticity evaluation.[34] We thus have chosen to calculate both the isotropic and the out-of-plane components of the chemical shielding tensor, denoted respectively as σ_{iso} and σ_{ZZ}, evaluated at the ring centers and 1.0 Å above, using the B3LYP/6-311G(d,p) wave functions and the GIAO[35−38] method as a convenient way of characterizing aromaticity.

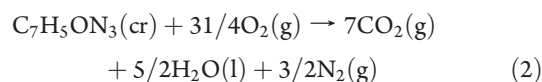All calculations were performed with the Gaussian 03 series of programs.[39]

4. RESULTS

4.1. Experimental Results. The results of the combustion experiments of 1,2,3-benzotriazin-4($3H$)-one are given in Table 1. As samples were ignited at T = 298.15 K[40]

$$\Delta U(IBP) = -\{\varepsilon_{cal} + c_p(H_2O,l)\Delta m(H_2O) + \varepsilon_f\}\Delta T_{ad} + \Delta U(ign) \quad (1)$$

where $\Delta U(IBP)$ is the energy associated with the isothermal bomb process, ε_{cal} is the energy equivalent of the calorimeter, $c_p(H_2O, l)$ is the specific heat capacity of liquid water, $\Delta m(H_2O)$ is the deviation of the mass of water added to the calorimeter from 3119.6 g, ε_f is the energy of the bomb contents after ignition, ΔT_{ad} is the adiabatic temperature increase calculated using the program LABTERMO,[41] and ΔU_{ign} is the energy of ignition. The remaining symbols in Table 1 have been previously described;[40] therefore, only a briefly description will be given here. The electrical energy for ignition $\Delta U(ign)$ was determined from the change in potential difference across the capacitor when discharged through the platinum ignition wire. For the cotton thread fuse of empirical formula $CH_{1.686}O_{0.843}$, the specific energy of combustion is $\Delta_c u° = -16240$ J·g^{-1},[42] a value previously confirmed in our laboratory. The corrections for nitric acid formation $\Delta U(HNO_3)$ were based on -59.7 kJ·mol^{-1}[43] for the molar energy of formation of 0.1 mol·dm^{-3} HNO_3(aq) from N_2(g), O_2(g), and H_2O(l). An estimated pressure coefficient of specific energy, $(\partial u/\partial p)_T = -0.2$ J·g^{-1}·MPa^{-1} at T = 298.15 K, a typical value for most solid organic compounds, was assumed.[44] The corrections to the standard state were made by the procedure given by Hubbard et al.[40] in order to obtain the value of the standard massic energy of combustion, $\Delta_c u°$.

The obtained mean value of the standard massic energy of combustion $\langle\Delta_c u°\rangle$ = −(24199.7 ± 4.0) J·g^{-1}, at T = 298.15 K, is referred to the combustion reaction

$$C_7H_5ON_3(cr) + 31/4O_2(g) \rightarrow 7CO_2(g) + 5/2H_2O(l) + 3/2N_2(g) \quad (2)$$

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The derived standard molar energy and enthalpy of combustion and the standard molar enthalpy of formation, in the solid phase, are respectively, $\Delta_c U_m^\circ(cr) = -(3560.6 \pm 1.6)$ kJ·mol^{-1}, $\Delta_c H_m^\circ(cr) = -(3558.7 \pm 1.6)$ kJ·mol^{-1}, and $\Delta_f H_m^\circ(cr) = (89.6 \pm 1.8)$ kJ·mol^{-1}. In accordance with normal thermochemical practices,[45] 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 $\Delta_f H_m^\circ$ from $\Delta_c H_m^\circ$, the standard molar enthalpy of formation for $CO_2(g)$, $-(393.51 \pm 0.13)$ kJ·mol^{-1}, and that for $H_2O(l)$, $-(285.830 \pm 0.042)$ kJ·mol^{-1}, were used.[46]

The standard molar enthalpy of sublimation at T = 298.15 K, $\Delta_{cr}^g H_m^\circ(298.15\,K) = (111.3 \pm 3.4)$ kJ·mol^{-1}, was derived from microcalorimetric measurements. The observed standard molar enthalpy $\Delta_{cr,298.15K}^{g,T} H_m^\circ$ determined from seven independent experiments at T = 436 K, (132.6 ± 3.4) kJ·mol^{-1} (the uncertainty is twice the standard deviation of the mean), was corrected to T = 298.15 K using the equation

$$\Delta_{298.15K}^T H_m^\circ(g) = \int_{298.15K}^T C_{p,m}^\circ(g)\,dT \qquad (3)$$

where T is the temperature of the hot reaction vessel and $C_{p,m}^\circ(g)$ is the molar heat capacity of gaseous 1,2,3-benzotriazin-4(3H)-one ($\Delta_{298.15K}^T H_m^\circ(g) = 21.3$ kJ·mol^{-1}). The heat capacity and its temperature dependence

$$C_{p,m}^\circ(g)/(J\cdot mol^{-1}\cdot K^{-1}) = -0.000346(T/K)^2$$
$$+ 0.651(T/K) - 37.193 \qquad (4)$$

were derived from statistical thermodynamics using the B3LYP/6-31G(d) vibrational frequencies obtained from the G3(MP2)//B3LYP calculations after correction for anharmonicity with the scale factor of 0.9613.[29]

By combining the values of the standard molar enthalpy of sublimation at T = 298.15 K and the standard enthalpy of formation in the solid phase at T = 298.15 K, we have derived the value of the standard enthalpy of formation of 1,2,3-benzotriazin-4(3H)-one in the gaseous phase at T = 298.15 K, $\Delta_f H_m^\circ(g) = (200.9 \pm 3.8)$ kJ·mol^{-1}.

4.2. Computational Results and Discussion. The molecular structures of 1,2,3-benzotriazin-4(3H)-one, the tautomer 1,2,3-benzotriazin-4(1H)-one, and the enol tautomer 1,2,3-benzotriazin-4-ol were fully optimized using the B3LYP hybrid functional and the 6-31G(d) and 6-311++G(d,p) basis sets. The bond lengths and angles obtained with the two basis sets do not differ significantly. The most relevant geometric parameters obtained with the more extended basis set are shown in Figure 1. In the Supporting Information (Table S1), we provide all of the geometrical parameters of the three structures and also experimental bond lengths and angles obtained from a X-ray diffraction study of the crystal structure of 1,2,3-benzotriazin-4(3H)-one.[16] The calculated geometrical parameters are generally in good agreement with the experimental values. The bond lengths obtained from our calculations differ at most by 0.024 Å from the experimental ones, while for the bond angles, differences of at most 2.2° are observed.

The three tautomers have completely planar structures; all of the atoms of the benzenic ring and the heterocyclic ring are located in the same plane. This fact could be anticipated because both rings are composed of sp^2-hybridized atoms. Indeed, it is
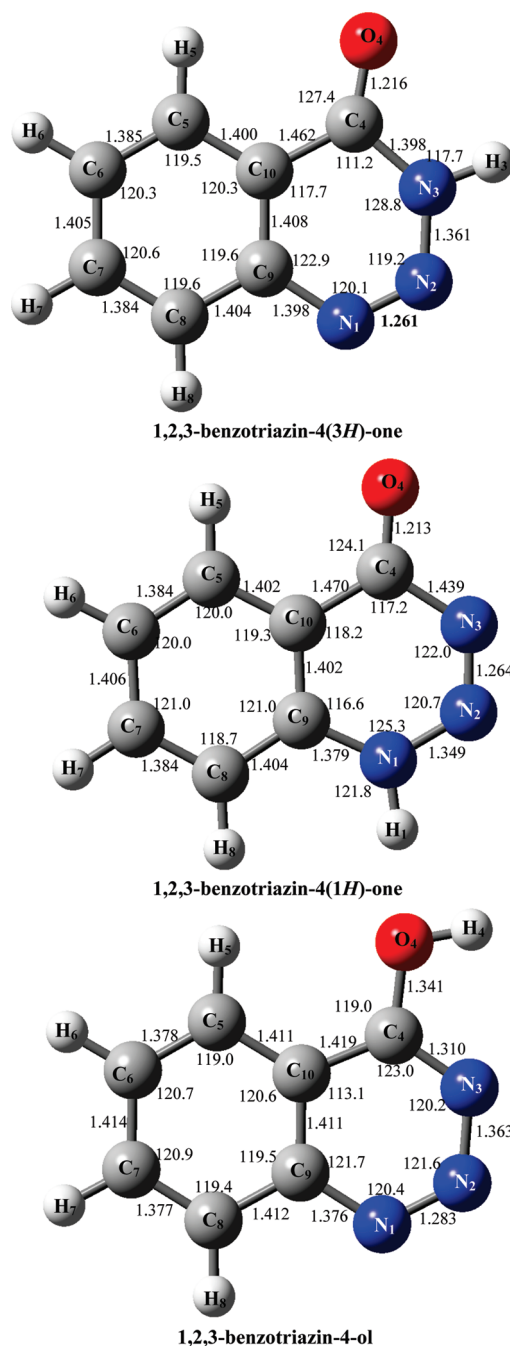
Figure 1. B3LYP/6-311++G(d,p) molecular structure of 1,2,3-benzotriazin-4(3H)-one, 1,2,3-benzotriazin-4(1H)-one, and 1,2,3-benzotriazin-4-ol. Bond lengths are in Å, and angles are in degrees.

this planar structure that favors the occurrence of electronic delocalization involving the two rings. Classical description of those systems in terms of resonance structures results in Lewis structures that grant two double bonds within the heterocyclic ring perfectly conjugated with the π electronic system of the benzenoid ring in the case of 1,2,3-benzotriazin-4-ol, while no such perfect conjugation can be achieved for 1,2,3-benzotriazin-4(3H)-one and 1,2,3-benzotriazin-4(1H)-one. This fact may imply a meaningful drop in the aromaticity of the heterocyclic ring of the latter systems when compared to that of 1,2,3-benzotriazin-4-ol, as we will find later on the basis of the analysis of their magnetic

**Table 2. Calculated B3LYP/6-311++G(d,p) Energies and Enthalpies and Relative Enthalpy Values**

	B3LYP/6-311++G(d,p)		
tautomer	E/au	H/au^a	ΔH/kJ·mol^{-1}
1,2,3-benzotriazin-4(3H)-one	−509.337944	−509.337000	0.0
1,2,3-benzotriazin-4(1H)-one	−509.318712	−509.317768	50.5
1,2,3-benzotriazin-4-ol	−509.317004	−509.316060	55.0

^{a} Enthalpies values, at T = 298.15 K, calculated using B3LYP/6-31G(d) thermal energy corrections.

Table 3. Computed G3(MP2)//B3LYP and Experimentally Determined Standard Molar Enthalpy of Formation of 1,2,3-Benzotriazin-4(3H)-one in the Gaseous Phase at T = 298.15 K

	$\Delta_f H_m^\circ(g)$/kJ·mol^{-1}			
	G3(MP2)//B3LYP			
compound	eq 5	eq 6	eq 7	experimental value
1,2,3-benzotriazin-4(3H)-one	194.2 (6.7)	200.1 (0.8)	197.0 (3.9)	200.9 ± 3.8

properties. In the most stable conformation of the enol tautomer, the O−H is directed toward the nitrogen atom, also favoring the formation of an intramolecular hydrogen bond (O−H···N).

In Table 2, we present the B3LYP/6-311++G(d,p) energies and enthalpies obtained for the three tautomers. As can be seen from this table, the calculations predict 1,2,3-benzotriazin-4(3H)-one to be energetically more stable than the tautomer 1,2,3-benzotriazin-4(1H)-one by about 50.0 kJ·mol^{-1} and also more stable than the enol tautomer by 55.0 kJ·mol^{-1}, this being, indeed, the least-stable tautomer that maintains the aromatic sextet within the carbocyclic ring. The amount of the observed energy differences guarantees that only the most stable tautomer needs to be considered in our thermochemical study because the other less-stable tautomers are predicted to be negligibly populated according to the Boltzmann distribution law.

In order to obtain accurate estimates of the enthalpy of formation of 1,2,3-benzotriazin-4(3H)-one in the gaseous phase at T = 298.15 K, we have also performed G3(MP2)//B3LYP calculations for this tautomer and for the atoms and molecules involved in the following reactions
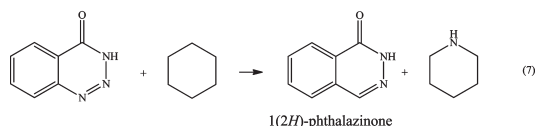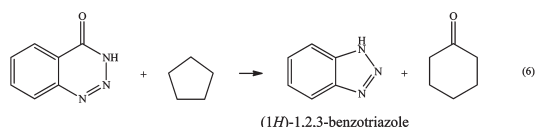
Reaction 5 is the atomization reaction of 1,2,3-benzotriazin-4(3H)-one, reaction 6 is an isodesmic reaction, and reaction 7 is an almost isodesmic reaction. The computational estimates of the enthalpy of formation of 1,2,3-benzotriazin-4(3H)-one were obtained from the calculated G3(MP2)//B3LYP reaction enthalpies and the experimental enthalpies of formation of each atom or molecule used in the reaction, except for the molecule for which we want to estimate the enthalpy of formation. Experimental enthalpies of formation were taken from Pedley's compendium,[47] except for the atoms[48] and 1(2H)-phthalazinone.[49] Calculated G3(MP2)//B3LYP enthalpies and experimental enthalpies of formation are given in the Supporting Information (Table S2). The computational estimates, presented in Table 3, are in very good agreement with the experimental value, the maximum

deviation being only 6.7 kJ·mol^{-1}, and this was obtained with the atomization reaction. It must be noted that for this reaction, which is as far as possible from being isodesmic, the cancellation of correlation errors is generally very crude. The best estimate was obtained with the isodesmic reaction. In this case, the computational estimate falls within the experimental uncertainty, while with the almost isodesmic reaction, there is a deviation of only 3.9 kJ·mol^{-1}.

The calculated components of the chemical shielding tensors are collected in Table 4. From these values, we can observe that, while the benzenoid rings of all molecules show NICS values that are typical of truly aromatic systems, the corresponding heterocyclic rings behave quite differently. Indeed, a large drop in the aromatic character is observed for the heterocyclic rings of 1,2,3-benzotriazin-4(3H)-one and 1,2,3-benzotriazin-4(1H)-one as compared to the analogous ring of (1H)-1,2,3-benzotriazole. In fact, in those cases, only the out-of-plane components of the chemical shielding tensors probed at the +1.0 Å points allow us to attribute to the heterocyclic rings a very moderate aromatic character. This fact occurs because, despite the presence within those rings of π-electronic systems satisfying the Huckel rule count of six electrons, true and complete circular delocalization is prevented by the presence of the carbonyl group, which contributes no π-electrons to that system, thus breaking the continuity. On the contrary, for 1,2,3-benzotriazin-4-ol and 1,2,3-benzotriazole, the calculated NICS values indicate much more aromatic heterocyclic rings.

Considering that 1,2,3-benzotriazin-4(3H)-one is analogous to 1(2H)-isoquinolinone, the difference being the change of −N=N− to −CH=CH−, and likewise the 1,2,3-benzotriazin-4(1H)-one isomer is analogous to 4(1H)-quinolinone, the following reaction should be expected to be approximately thermoneutral
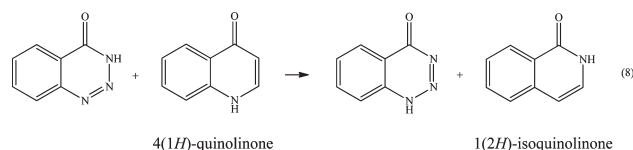

Indeed, from G3(MP2)//B3LYP calculations, we obtained a value of 7.6 kJ·mol^{-1} for the enthalpy of the above reaction. This is due to the fact that the calculated enthalpy of formation difference of 1,2,3-benzotriazin-4(3H)-one and its (1H)-isomer, 49.2 kJ·mol^{-1}, is approximately equal to the difference of the enthalpies of formation of 1(2H)-isoquinolinone and 4(1H)-quinolinone, 41.6 kJ·mol^{-1}. In fact, 1(2H)-isoquinolinone and 4(1H)-quinolinone are experimentally found as their 1-hydroxyisoquinoline and 4-hydroxyquinoline tautomers, and therefore, the measured enthalpies of formation for these species,

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Table 4. Isotropic (σ_{iso}) and out-of-Plane (σ_{ZZ}) Components of the Chemical Shielding Tensor Measured at the Center (0) and 1.0 Å above the Center of the Benzenic and the Heterocyclic Rings (all values in ppm)

	benzenic ring				heterocyclic ring			
	0		+1		0		+1	
compound	σ_{iso}	σ_{ZZ}	σ_{iso}	σ_{ZZ}	σ_{iso}	σ_{ZZ}	σ_{iso}	σ_{ZZ}
1,2,3-benzotriazin-4(3H)-one	−9.63	−13.59	−11.40	−28.51	+0.46	+14.66	−4.31	−7.08
1,2,3-benzotriazin-4(1H)-one	−9.40	−11.08	−10.76	−26.39	+2.13	+17.50	−3.29	−4.85
1,2,3-benzotriazin-4-ol	−9.58	−13.61	−11.61	−29.15	−5.02	−3.87	−9.92	−22.58
(1H)-1,2,3-benzotriazole	−10.35	−14.37	−11.62	−29.46	−13.56	−15.15	−13.30	−33.66
benzene	−8.90	−14.52	−11.13	−29.31				

respectively, $-(33.2 \pm 2.9)$ kJ·mol^{-1} [50] and (20.8 ± 2.3) kJ·mol^{-1},[51] could not be used directly in the current study.

We may also briefly discuss the stability of the tautomeric 1,2,3-benzotriazin-4-ones in terms of language derived from a recent model[21] for the aromaticity of derivatives of indane and indene, species with benzene-fused five-membered rings. For these latter species, we suggested the use of the reaction

$$C_6H_4XYZ + 2C_2H_6 \rightarrow o\text{-}C_6H_4(CH_3)_2 + CH_3XYZCH_3$$
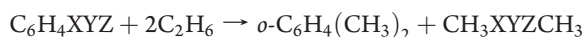
By analogy, we would write

$$C_6H_4WXYZ + 2C_2H_6 \rightarrow o\text{-}C_6H_4(CH_3)_2 + CH_3WXYZCH_3$$

To the extent that thermochemical data for species of the CH$_3$XYZCH$_3$ are often absent, we are a fortiori thwarted for many cases where CH$_3$WXYZCH$_3$ is to be discussed should we seek quantitation. Nonetheless, we recognize these acyclic fragments corresponding to 1,2,3-benzotriazin-4(3H)-one and 1,2,3-benzotriazin-4(1H)-one as acylamine (amides) and acylimine derivatives. As such, the former heterocycle is expected to be of considerably greater stability than the latter,[52] a finding that corroborates our calculational finding of isomeric stability of the 3- and 1H-benzotriazinones. This is reminiscent of the greater stability of coumarin $-(163.4 \pm 3.3)$ kJ·mol^{-1} [19] relative to chromone $-(126.1 \pm 2.5)$ kJ·mol^{-1} [19] because the former is an ester while the latter is "merely" a β-acylated vinyl ether.[53]

Coumarin   Chromone
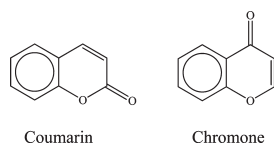
In a similar way, we explain the greater stability of 3-isochromanone, $-(236.4 \pm 2.3)$ kJ·mol^{-1} [20] and dihydrocoumarin, $-(248.9 \pm 2.3)$ kJ·mol^{-1},[20] relative to chromanone, $-(204.5 \pm 2.4)$ kJ·mol^{-1},[20] as due to the fact the former two isomers are esters while the latter is a considerably less stabilized γ-keto-alkyl ether.

3-Isochromanone   Dihydrocoumarin   Chromanone
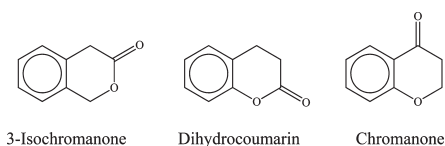
5. CONCLUSIONS

A combined experimental and computational study has been performed for 1,2,3-benzotriazin-4(3H)-one and respective tautomers 1,2,3-benzotriazin-4(1H)-one and 1,2,3-benzotriazin-4-ol in

order to understand the interrelations between structure and energetics. Experimentally, we have used combustion calorimetry to determine the standard molar enthalpy of formation in the solid phase of 1,2,3-benzotriazin-4(3H)-one. The respective standard molar enthalpy of sublimation was determined using Calvet microcalorimetry. These two thermodynamic parameters allowed the calculation of the standard molar enthalpy of formation in the gas phase of 1,2,3-benzotriazin-4(3H)-one at $T =$ 298.15 K. Quantum chemical calculations predict 1,2,3-benzotriazin-4(3H)-one to be the most stable tautomer. The standard molar enthalpy of formation estimates obtained with the G3-(MP2)//B3LYP method are in very good agreement with the experimentally determined value. NICS values indicate that the heterocyclic rings of the keto tautomers have very moderate aromatic character, while the one of the enol tautomer has a much more aromatic character in relation to benzene.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. B3LYP/6-311++G(d,p) geometrical parameters for 1,2,3-benzotriazin-4(3H)-one and the tautomers 1,2,3-benzotriazin-4(1H)-one and 1,2,3-benzotriazin-4-ol and G3(MP2)//B3LYP absolute enthalpies and experimental standard molar enthalpies of formation in the gaseous phase at T = 298.15 K for 1,2,3-benzotriazin-4(3H)-one, 1,2,3-benzotriazin-4(1H)-one, 1,2,3-benzotriazin-4-ol, and auxiliary atoms and molecules used in this study. This material is available free of charge via the Internet at http://pubs.acs.org.

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