Improved synthesis and thermochemical properties of amino- and hydrazino-1,2,4,5-tetrazines

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Improved protocols for the synthesis of 3,6-diamino- and 3,6-dihydrazino-1,2,4,5-tetrazines as well as 6-amino[1,2,4]triazolo[4,3-*b*]-[1,2,4,5]tetrazine were developed. Combustion energies were determined by the bomb calorimetry and the enthalpies of formation in the standard state were calculated for the compounds of this study. Based on the obtained data, the contribution of the 1,2,4,5-tetrazine moiety to the enthalpy of combustion of its derivatives was estimated.

Keywords: 1,2,4,5-tetrazine, calorimetry, enthalpy of combustion, enthalpy of formation.

Precise experimental values of the enthalpies of formation $(\Delta H_{\rm f})$ of compounds of various classes undoubtedly form the basis of fundamental thermochemistry and are also of great importance for applied science. Unfortunately, experimental values are available for less than 0.1% of known compounds. Since the experimental determination of thermochemical characteristics is a very laborious process, significant efforts are spent on the development of computational approaches. Various empirical and semiempirical methods require extensive parametrization and often lead to significant errors in the assessment of atypical molecules, in particular energy-rich molecules which are components of energetic materials (explosives, propellants, pyrotechnic compositions).

When assessing the potential value of an energetic compound, the key performance indicators are usually the detonation velocity and pressure for explosives, and the specific impulse for propellants. The basic characteristic that determines these properties is the energy that is released during detonation or combustion which can be easily estimated by calculation methods¹ if the heat of formation of the compound $\Delta H_{\rm f}$ is known.² The decomposition energy is also related to the sensitivity of

energetic compounds to the initiation of detonation³ characterizing the risks of their use. Only having a reliable $\Delta H_{\rm f}$ value the performance and the safety of using an energetic compound can be correctly assessed.

High nitrogen heterocycles are the most promising and environmentally attractive building blocks for designing new energetic compounds. Indeed, compounds with a high nitrogen content are characterized by high energy content, and their decomposition is accompanied by the release of a large amount of heat and the formation of environmentally friendly molecular nitrogen as the main product of destruction.⁴

In recent years, the possibilities for the design of energetic compounds based on 1,2,4,5-tetrazine have been demonstrated.⁵ However, the information available in the literature on the experimentally measured values of the enthalpies of formation of derivatives of this heterocycle is very scarce.⁶ Here, the results of a thermochemical study of three tetrazine derivatives: 3,6-diamino-1,2,4,5-tetrazine (1), 3,6-dihydrazinyl-1,2,4,5-tetrazine (2) (Scheme 1), and 6-amino[1,2,4]triazolo[4,3-*b*][1,2,4,5]tetrazine (3) (Scheme 2), already widely used⁵ in the practical chemistry of energetic compounds are described.





We measured the combustion energies of compounds 1–3 by bomb calorimetry and calculated the enthalpies of their formation in the standard state. Based on the obtained thermochemical data, the contribution of the 1,2,4,5tetrazine moiety to the enthalpy of combustion of its derivatives was calculated. Note that obtaining precision experimental values of the standard enthalpies of formation in the solid phase $\Delta H^{\circ}_{f}(cr)$, complementing the existing database, makes it possible to increase the accuracy of estimating the enthalpies of formation of hypothetical analogs by the group contribution method, which combines simplicity and reliability.

Despite the fact that compounds 1-3 have been known for a long time, the methods of their synthesis are not effective or use expensive reagents. We began our studies by developing more effective synthetic protocols. The most widely used precursor in the synthesis of 1,2,4,5-tetrazine derivatives (also called *s*-tetrazine) is 3,6-bis(3,5dimethylpyrazol-1-yl)-*s*-tetrazine (**4**).⁷

The dimethylpyrazolyl groups of compound **4** can be replace by the action of various nucleophiles which is widely employed in organic synthesis to obtain tetrazine-containing compounds.⁸ It is known that the introduction of an electron-withdrawing moiety, such as a bromine or chlorine atom, into position 4 of the pyrazole facilitates the substitution of this modified substituent with nucleophiles.⁹ Assuming that the presence of a nitro group in the pyrazole ring will further increase the nucleofugicity of the leaving group, we synthesized nitro derivative **5** by treating compound **4** with a mixture of 100% HNO₃ and trifluoroacetic anhydride (Scheme 1).

As is known, the substitution of two pyrazole moieties in tetrazine **4** with amino groups proceeds only at treatment with an excess of NH₃ in *N*-methylpyrrolidone (NMP) at 90°C in an autoclave under pressure (10 atm) for 6 h.⁷ We found that the substitution of the nitropyrazole moiety of compound **5** is easily accomplished with an excess of aqueous NH₃ in glyme at room temperature and ordinary pressure for 1 h, giving diamine **1** in 97% yield (Scheme 1). When a solution of compound **5** in glyme was treated with

hydrazine hydrate, both nitropyrazole moieties were instantly substituted at room temperature and 3,6dihydrazinyl-s-tetrazine (2) was formed in quantitative yield (Scheme 1).

The synthesis route for compound 3 was also simplified (Scheme 2). The most problematic step in the synthesis of compound 3 is the 1,2,4-triazole ring closure which leads to the formation of the bicyclic product 7. Earlier, expensive diethoxymethyl acetate was used to cyclize the readily available monohydrazinyl derivative 6, and, as a result of heating the reaction mixture under reflux for 5 min, compound 7 was formed in 93% yield.¹⁰ Later it was reported that heating monohydrazine 6 with an excess of cheaper triethyl orthoformate under reflux for 3 h affords product 7 in 72% yield.¹¹ We have shown that the addition of trifluoroacetic acid to triethyl orthoformate makes it possible to carry out the reaction at room temperature in 1 h (70% yield), whereas at 70°C it is complete in 5 min leading to product 7 in 94% yield. The substitution of the pyrazole moiety of compound 7 was carried out according to the literature method in boiling EtOH using 30% aqueous ammonia, which made it possible to obtain crude compound 3 in 77% yield in 2 h.¹⁰ Analytically pure sample 3 was obtained in 58% yield.



The developed methods scale up well, which allows one to obtain the compounds of this study in the required quantities. For thermochemical study, the samples were purified by repeated recrystallization and vacuum drying. The structures and purity of the synthesized compounds were confirmed by ¹H and ¹³C NMR spectroscopy, mass spectrometry, and elemental analysis.

The energies of combustion as measured by bomb calorimetry for the compounds of this study are given in Table 1. Reactions of combustion of compounds 1-3 proceed in accordance with the stoichiometry presented by equations (1)–(3), respectively:

$$\begin{array}{ll} C_2H_4N_{6(cr)}+3O_{2(g)}=2CO_{2(g)}+2H_2O_{(l)}+3N_{2(g)}, & (1) \\ C_2H_6N_{8(cr)}+3.5O_{2(g)}=2CO_{2(g)}+3H_2O_{(l)}+4N_{2(g)}, & (2) \end{array}$$

$$C_{3}H_{3}N_{7(cr)} + 3.75 O_{2(g)} = 3CO_{2(g)} + 1.5H_{2}O_{(l)} + 3.5N_{2(g)},$$
 (3)

where the subscripts cr, g, and l correspond to the crystalline, gaseous, and liquid states, respectively.

Test	m_o	ΔT	Q	$q_{ m a}$	$q_{ m i}$	$q_{ m N}$	$q_{ m cot}$	$-\Delta U_{ m B}$
			Co	mpound 1				
1	0.100831	2.13457	1144.19	757.13	0.524	4.42	6.74	3544.3
2	0.075659	1.89702	1016.86	739.84	0.524	2.07	6.07	3546.9
3	0.074610	1.96027	1050,76	776.39	0.524	2.04	7.12	3547.6
4	0.119840	2.23241	1196.64	760.49	0.524	4.49	6.04	3547.2
							$-\Delta U'_{\rm B} = 3$	$546.5 \pm 2.1 \text{ cal} \cdot \text{g}^{-1}$
			Co	mpound 2				
1	0.076797	2.35093	1263.84	989.80	3.824	2.35	7.49	3650.9
2	0.071023	2.33160	1253.44	980.26	3.824	2.21	7.61	3654.3
3	0.079823	2.42102	1301.52	995.26	3.824	2.51	8.36	3652.6
4	0.081317	2.40201	1291.30	979.78	3.824	2.54	8.17	3652.2
5	0.081924	2.42271	1302.42	988.81	3.824	2.58	7.75	3655.4
							$-\Delta U'_{\rm B} = 3$	$653.1 \pm 2.0 \text{ cal} \cdot \text{g}^{-1}$
			Co	mpound 3				
1	0.075299	1.86283	989.42	707.43	0.524	2.62	6.58	3615.8
2	0.084248	2.02763	1076.96	761.76	0.524	2.95	7.37	3612.6
3	0.081874	2.42706	1304.76	997.54	0.524	2.86	7.69	3617.1
4	0.080778	2.38783	1283.67	980.09	0.524	2.82	8.21	3615.2
5	0.081228	2.39929	1289.83	984.21	0.524	2.84	8.35	3618.3
							$-\Delta U'_{\rm B} = 3$	$615.8 \pm 2.5 \text{ cal} \cdot \text{g}^{-1}$

Table 1. Combustion energies of tetrazines 1-3*

* The notation used: m_0 – weight of the sample of the test compound in vacuum, g; ΔT – corrected temperature rise in the calorimeter, degrees; Q – the amount of heat measured in a test, cal; q_a – heat of the combustion of the auxiliary compound benzoic acid, cal; q_i – ignition energy, cal; q_N – correction for the formation of nitric acid, cal; q_{cot} – heat generation from combustion of the cotton thread, cal; ΔU_B – combustion energy of a compound in the bomb, cal $\cdot g^{-1}$.

The enthalpies of formation of tetrazines 1-3 were calculated based on the enthalpies of combustion using equations (4)–(6), respectively:

$$\Delta H^{o}_{f}[C_{2}H_{4}N_{6}]_{(cr)} = 2\Delta H^{o}_{f}[CO_{2}]_{(g)} + 2\Delta H^{o}_{f}[H_{2}O]_{(l)} + + 3\Delta H^{o}_{f}[N_{2}]_{(g)} - \Delta H^{o}_{c}, \qquad (4)$$

$$\Delta H^{o}_{f}[C_{2}H_{6}N_{8}]_{(cr)} = 2\Delta H^{o}_{f}[CO_{2}]_{(g)} + 3\Delta H^{o}_{f}[H_{2}O]_{(l)} + + 4\Delta H^{o}_{f}[N_{2}]_{(g)} - \Delta H^{o}_{c},$$
(5)

$$\Delta H^{0}_{f}[C_{3}H_{3}N_{7}]_{(cr)} = 3\Delta H^{0}_{f}[CO_{2}]_{(g)} + 1.5\Delta H^{0}_{f}[H_{2}O]_{(l)} + 3.5\Delta H^{0}_{f}[N_{2}]_{(g)} - \Delta H^{0}_{c}, \qquad (6)$$

where ΔH°_{c} – the standard enthalpy of combustion of the corresponding compound, kcal·mol⁻¹, and ΔH°_{f} – the standard enthalpy of its formation, kcal·mol⁻¹.

When calculating the standard enthalpies of formation of the compounds of this study, we used the reference values of the enthalpies of formation of combustion products: $\Delta H^{o}_{f}[CO_{2}]_{(g)} = -94.051 \pm 0.031$ and $\Delta H^{o}_{f}[H_{2}O]_{(l)} = -68.315 \pm 0.009 \text{ kcal} \cdot \text{mol}^{-1}.^{12}$ Table 2 compiles the obtained thermochemical characteristics of the compounds of this study.

Based on the obtained values of thermochemical parameters, the contribution of the 1,2,4,5-tetrazine moiety to the enthalpy of combustion in the standard state was estimated using the values of thermochemical contributions to the enthalpy of combustion of amino and hydrazino groups (-84.1 and -144.6 kcal·mol⁻¹, respectively; determined from benzene derivatives¹³). This contribution, calculated from the thermochemical parameters of compound **1**, was -228.0 kcal·mol⁻¹ (which corresponds to -2.85 kcal·g⁻¹) and differs only by 0.1 kcal from the value obtained from the calculation from the enthalpy of

 Table 2. Enthalpies of combustion and formation of 1,2,4,5-tetrazine derivatives 1–3

Compound	$-\Delta H^{\rm o}_{\rm c},$ kcal·mol ⁻¹	$\Delta H^{\rm o}{}_{\rm f},$ kcal·mol ⁻¹		
1	395.9 ± 0.2	71.2 ± 0.2		
2	517.3 ± 0.3	124.3 ± 0.3		
3	493.7 ± 0.3	108.9 ± 0.3		

combustion of compound **2**, confirming the accuracy of the estimate.

We have previously shown that the contribution of the [1,2,4]triazolo[4,3-b][1,2,4,5]tetrazine moiety, calculated on the basis of the enthalpies of combustion of its 3-(3-R-furazanylamino) derivatives, is -409.0 kcal·mol^{-1.6d} The contribution of this moiety, based on the enthalpy of combustion of compound **3**, is -409.6 kcal·mol⁻¹, that is, it is in good agreement with the value published previously.

The obtained data can be used to assess the enthalpy characteristics of compounds containing 1,2,4,5-tetrazine and [1,2,4]triazolo[4,3-b][1,2,4,5]tetrazine moieties.

In conclusion, it should be noted that recently the enthalpy of formation of compound **3** was calculated using B3LYP and B3P86 with the 6-311G** basis set.¹⁴ According to calculations, this value was 148.16 and 146.21 kcal·mol⁻¹, respectively. As one can see, the calculated values are significantly overestimated (compare with Table 2). Since the enthalpy of formation of a compound is a key parameter in the calculations of all important characteristics of energetic materials, the use of incorrect starting data leads to fatal errors.

Experimental

IR spectra were registered on a Bruker Alpha spectrometer in KBr pellets. ¹H, ¹³C, and ¹⁴N NMR spectra were acquired on a Bruker AM-300 (300, 75, and 21 MHz, respectively) in DMSO- d_6 . Chemical shifts of ¹H and ¹³C nuclei are given relative to TMS, for ¹⁴N nuclei – relative to MeNO₂. Mass spectra were recorded on a Finnigan MATINCOS 50 mass spectrometer (direct sample injection, EI ionization, 70 eV). Elemental analysis was performed on a PerkinElmer Series II 2400 CHN-analyzer. Melting points were determined on a Gallenkamp heating bench and are uncorrected. Monitoring of the reaction progress and assessment of the purity of synthesized compounds were done by TLC on Sorbfil 60 F₂₅₄ plates.

The starting compound **4** was obtained according to a literature method.⁷

3,6-Bis(3,5-dimethyl-4-nitropyrazol-1-yl)-1,2,4,5-tetrazine (5). Concentrated HNO₃ ($d \ 1.5 \ \text{g/cm}^3$) (4 ml) was added dropwise to a cooled (-10°C) trifluoroacetic anhydride (11.2 ml). The resulting solution was kept at -10° C for 0.5 h, then cooled to -30°C, and anhydrous MeCN (20 ml) was added dropwise. Tetrazine 4 (0.6 g, 2.2 mmol) was added, and the mixture was allowed to warm up to room temperature. The reaction mixture was stirred for an additional 15 min at room temperature and poured onto ice. The precipitate was filtered off, washed with H_2O (3×15 ml) and *i*-PrOH (5 ml), air-dried, and crystallized from MeCN. Yield 0.78 g (98%), pink amorphous powder, mp 284–286°C. IR spectrum, v, cm⁻¹: 1576, 1516, 1504, 1452, 1436, 1412, 1380, 1348, 1176, 1132, 1064, 1036, 996, 940, 848, 792, 764. ¹H NMR spectrum, δ , ppm: 2.40 (12H, br. s, 4CH₃). ¹³C NMR spectrum, δ, ppm: 12.2; 13.8; 132.4; 143.5; 147.3; 152.3. ¹⁴N NMR spectrum, δ, ppm: -14.4 (NO₂). Mass spectrum, m/z (I_{rel} , %): 360 [M]⁺ (19), 167 (28), 149 (47), 121 (100), 93 (67), 80 (53), 67 (82), 53 (61), 39 (72). Found, %: C 40.08; H 3.41; N 38.78. C₁₂H₁₂N₁₀O₄. Calculated, %: C 40.00; H 3.36; N 38.88.

3,6-Diamino-1,2,4,5-tetrazine (1). 33% Aqueous NH₃ (30 ml) was added with stirring at room temperature to a suspension of compound **5** (5 g, 0.014 mol) in glyme (30 ml). A precipitate formed from the resulting solution after about 1 h of stirring. The precipitate was filtered off, washed with a CCl₄–*i*-PrOH, 5:1 mixture, and dried in air. Yield 1.9 g (97%), fine red-brown crystals, mp 300°C (decomp.) (mp > $350^{\circ}C^{15}$). Physicochemical and spectral characteristics of the product are identical to those described in the literature.¹⁶ Found, %: C 21.47; H 3.65; N 74.92. C₂H₄N₆. Calculated, %: C 21.43; H 3.60; N 74.97.

3,6-Dihydrazino-1,2,4,5-tetrazine (2). N_2H_4 · H_2O (0.5 g, 0.01 mol) was added dropwise at room temperature to a vigorously stirred solution of compound **5** (1.8 g, 0.005 mol) in glyme (20 ml), and after 5 min the resulting mixture was cooled to 0°C. The precipitate was filtered off, washed with a CCl₄–*i*-PrOH, 5:1 mixture, and dried in air. Yield of product **2** 1.7 g (98%), red-brown solid, mp 160–162°C (decomp.), identical in all respects to that described in the literature.¹⁰ Found, %: C 16.97; H 4.27; N 78.78. C₂H₆N₈. Calculated, %: C 16.90; H 4.26; N 78.84.

3-(3,5-Dimethyl-1*H***-pyrazol-1-yl)[1,2,4]triazolo[4,3-***b***]-[1,2,4,5]tetrazine (7). Trifluoroacetic acid (5 ml, 0.067 mol) was added dropwise to a suspension of compound 6** (4.12 g, 0.02 mol) in triethyl orthoformate (20 ml, 0.15 mol). In this case, the mixture spontaneously heated up to 40°C, and a solution was formed. After about half of the trifluoroacetic acid has been added, a yellow amorphous precipitate began to form. The reaction mixture was heated to 70°C and allowed to cool. The formed precipitate was filtered off, washed with aqueous *i*-PrOH, and dried. Yield 4.06 g (94%), bright-yellow amorphous substance, mp 241–243°C (mp 246–247°C,¹⁰ mp 248°C¹¹). Spectral characteristics of the product are identical to those described in the literature.¹⁰ Found, %: C 44.50; H 3.77; N 51.75. C₈H₈N₈. Calculated, %: C 44.44; H 3.73; N 51.83.

[1,2,4]Triazolo[4,3-b][1,2,4,5]tetrazin-6-amine (3). Compound 7 (0.54 g, 2.5 mmol) was added to a mixture of 8% aqueous NH₄OH (15 ml) and EtOH (20 ml). The reaction mixture was heated under reflux for 2 h, after which half of the solvent was evaporated. The residue was extracted with CH₂Cl₂ (2×15 ml) to separate dimethylpyrazole. *i*-PrOH (5 ml) was added to the aqueous phase. The resulting mixture was left in the refrigerator overnight. The next day, the formed precipitate was filtered off and airdried. The product was recrystallized from H₂O, which, according to the literature,¹⁰ led to the formation of the monohydrate of the product with mp 217-218°C (H₂O). The substance was dried to constant weight in a drying oven at 100–110°C (~24 h), which afforded the anhydrous vellow amorphous product 3. Yield 0.2 g (58%), mp 186-189°C (decomp.). IR spectrum, v, cm⁻¹: 3393, 3136, 3038, 2853, 1680, 1550, 1443, 1414, 1368, 1325, 1139, 1050, 970, 944, 872, 836, 761, 711, 696, 670. Mass spectrum, m/z $(I_{\rm rel}, \%)$: 137 $[M]^+$ 121, 98, 95, 86, 82, 77, 67, 57, 56, 55, 44. Found, %: C 26.31; H 2.23; N 71.47. C₃H₃N₇. Calculated, %: C 26.28; H 2.21; N 71.51. According to the ¹H and ¹³C NMR spectra, the compound was identical to that described in the literature.¹⁰

Calorimetric measurements. The combustion energies for the compounds of this study were determined on a precision automatic combustion calorimeter with an isothermal shell (designed by the Laboratory of thermodynamics of energetic compounds of the Institute of Chemical Physics of the Russian Academy of Sciences), developed specifically for the study of energetic materials.¹⁷ Samples of the studied compounds (usually from 0.07 to 0.12 g) were weighed in a platinum crucible and placed into the bomb of the calorimeter which was then filled with oxygen. The initial oxygen pressure during combustion of all compounds was about 3 MPa. Before the experiment, distilled H₂O (1 ml) was injected into the bomb to create a saturated vapor pressure and dissolve nitrogen oxides formed during combustion. A detailed procedure for the preparation of the sample and the combustion experiment has been described earlier.¹⁵

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